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Determination of Sulphur Present as Sulphide in Portland Cement.

By D. IRVINE WATSON, B.Sc., A.I.C.

IT sometimes happens during the burning of Portland cement that a small amount of sulphur present in the fuel escapes oxidation and is left in the form of sulphide in the finished cement. In view of the fact that this somewhat unstable form of sulphur, if present to any appreciable extent, may produce undesirable results at a later date, it is necessary to have a reliable method for the direct determination of the amount of sulphur present as sulphide in Portland cement.

The usual evolution methods fail because Portland cement contains readily soluble iron compounds in the ferric state which, upon the addition of dilute hydrochloric acid, immediately react with the H_2S formed, and with any undecomposed sulphides, according to the equations

$$2FeCl_3 + H_2S = 2HCl + 2FeCl_2 + S \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$
$$8FeCl_3 + 4H_2O + H_2S = 8HCl + H_2SO_4 + 8FeCl_2 \quad \ldots\ldots\ldots \quad (2)$$

Effect of Fe^{III} ion concentration on results given by a typical evolution method.—To 5 gms. of cement free from sulphide 0.0108 gm. of sulphur in the form of sodium sulphide was added: weight of sulphur evolved, 0.0037 gms. To 10 gms. of the same cement 0.0108 gm. of sulphur in the form of sodium sulphide was added: weight of sulphur evolved, 0.0021 gms.

In spite of the uncertainty always felt in the use of indirect methods, the method in most common use at present is to determine the percentage of total sulphate present after oxidation with bromine in hydrochloric acid solution, or with aqua-regia, and then to deduct the percentage of sulphate determined in the usual way. This process, however, gives rise to a similar error, as the figure obtained for sulphate present is too high by the amount of sulphide oxidised by ferric chloride during the solution of the cement.

A convenient method of eliminating this inaccuracy is to add a considerable excess of stannous chloride solution to the cement before any attempt is made to liberate the H_2S by the addition of acid. This ensures that the iron is reduced to the ferrous state before it can have any appreciable oxidising effect on the sulphide present. Some modification of the normal evolution method is then

necessary to ensure that stannous sulphide is not left in the flask. The following method has given satisfactory results.

The apparatus consists of a wide-mouthed round-bottomed flask of 250 c.c. capacity fitted with a rubber bung bored with two holes, through one of which is passed the leg of a tap funnel of 70 c.c. capacity, and through the other a short Cribb's condenser. The top of the tap funnel is connected to a supply of hydrogen suitably freed from H_2S, and the outlet of the condenser to two conical flasks arranged in series for gas absorption. The function of the condenser is to prevent liquid from distilling into the absorption vessels.

A convenient cadmium chloride solution is made by dissolving 20 grm. of crystalline cadmium chloride ($CdCl_2 2\frac{1}{2}H_2O$) in 100 c.c. of 0.880 ammonia and 1 litre of water. Part of the water is added to the salt, then the ammonia, and finally the remainder of the water. It is filtered if necessary.

The stannous chloride solution is prepared by digesting a weighed piece of pure tin in a deficiency of hydrochloric acid (S.G. 1.165) until all action ceases. The tin is removed and reweighed, the loss in weight being considered as the amount of tin in solution. The liquid is filtered from any small amount of sludge, and the filtrate adjusted to such a volume that the solution obtained contains 10 grammes of tin (Sn) per 100 c.c.

For the determination, 5.0 grm. of cement is weighed into the flask; 10 c.c. of cadmium chloride solution, 40 c.c. of water, and a few drops of strong ammonia are placed in each of the absorption vessels. Ten c.c. of water are added to the cement in the flask, and the latter quickly shaken until the cement is thoroughly wetted without any sign of setting, then 10 c.c. of stannous chloride solution added, and after swirling the flask is placed in position. The apparatus is then connected up, and a current of hydrogen passed until all air is expelled. This should take about five minutes, but the issuing gas should be tested. The dropping funnel is then filled with hydrochloric acid solution, prepared by diluting 50 c.c. of concentrated hydrochloric acid (S.G. 1.165) with 20 c.c. of water, and the apparatus connected up again. The tap of the dropping funnel is opened and the acid allowed to run into the flask with the hydrogen still running, and when the funnel is empty the evolved H_2S is swept through the apparatus by the stream of hydrogen, and the action in the flask accelerated by applying heat until the liquid simmers. After five minutes gentle boiling the apparatus is allowed to cool, the current of hydrogen being continued all the while.

The first absorption vessel should now contain a precipitate of cadmium sulphide, while the second should be clear unless some of the gas has escaped by too rapid evolution. The cadmium sulphide is filtered off and washed once with cold water. Ten c.c. of water, together with 10 c.c. of concentrated hydrochloric acid (S.G. 1.165), are placed in the empty flask, and 10 c.c. of N/10 iodine solution added. It is essential that the solution should be acid before adding the iodine, otherwise any ammonia left with the cadmium sulphide will consume iodine. Into this acid liquid the filter paper and precipitate are dropped. The flask is then stoppered, shaken for one minute, and the excess of iodine determined by titration with N/10 thiosulphate and starch. The filter paper should be broken up during this process. One c.c. of N/10 thiosulphate solution = 0.0016 grm. S.

The essential variations from the usual evolution methods are: Reduction of iron by stannous chloride; use of more concentrated hydrochloric acid to ensure decomposition of stannous sulphide; larger bulk of liquid in flask to avoid trouble with gelatinous silica.

Comparisons between the results given by this method and a typical evolution method:—

(*a*) On two samples of cement containing sulphide as received in normal course of work.

	Percentage of Sulphur.	
	Stannous chloride method. Per cent.	Usual method. Per cent.
(1)	0.128	0.011
(2)	0.140	0.010

(*b*) On a sample of cement containing no sulphide, to which various definite amounts of sodium sulphide solution had been added.

Sulphur as sulphide added. Per cent.	Stannous chloride Method. Amount found. Per cent.	Usual method. Amount found. Per cent.
Nil	0.0016	0.0016=" Blank."
0.054	0.053	0.014
0.108	0.107	0.032
0.216	0.211	0.074

This method of determining sulphur as sulphide is published by the courtesy of Mr. R. H. Harry Stanger, for whom it was originally evolved by the writer.

Notes from Abroad.

Increase of Capital.

We understand that the S.A. des Ciments Portland de Lorraine has decided to increase its capital from 25,000,000 francs (£201,272) to 59,000,000 francs (£402,544).

Egyptian Import Duties.

The Egyptian Customs Law empowers the Government to impose a surtax equal to the amount of the customs duty on goods imported into Egypt from countries which have no commercial agreement with Egypt. By a Ministerial decree of November 3, 1931, this surtax has been applied to cement imported from the Soviet Union.

New Cement Plant in the United States.

We understand construction of the new plant of the Mississippi Portland Cement Company, Columbus, Miss., costing approximately $1,000,000 (£205,761), has recently been commenced. The annual capacity will be 1,000,000 barrels. This company was formed in September, 1930.

Dividends and Reports.

French Indo-China.—Société des Ciments Portland Artificiels de l'Indo-Chine has decided to pay an interim dividend of 10 francs gross, based on trading results for 1931. This compares with the interim dividend of 15 francs gross for the corresponding period of 1930.

France.—S.A. des Ciments Portland Artificiels de Cronfestu has declared a dividend of 35 francs for the year 1930-31, with a gross profit of 2,289,516 francs. This compares with a gross profit of 1,461,724 francs for the year 1929-30, when no dividend was paid.

Heat Economy in the Cement Industry.—II.

By Dr. HANS BUSSMEYER.

Two fundamentally different kilns are used in the modern cement industry, *viz.*, the shaft kiln and the rotary kiln.

A.—The Automatic Shaft Kiln.

The automatic shaft kiln has been evolved from the old-fashioned shaft kiln, which was periodically fed by hand. In the course of several decades it has been developed into a thoroughly reliable kiln of low fuel consumption, capable of producing, in the hands of an experienced burner, a clinker which, although not uniform, is generally satisfactory. The old shaft kiln needed, however, the most careful attention, and as the outputs required in the industry increased, and as the rise in wages made it necessary to reduce labour costs, this type of kiln more and more failed to fulfil the requirements of cement manufacturers. If it had not been possible to increase the kiln output—with the old type of kiln it was hardly possible to produce more than 20 tons of good clinker in 24 hours—and to reduce or entirely exclude manual operation, the cement industry would have been compelled to adopt some other type of kiln which fulfilled these two basic conditions, even at the cost of a considerably higher fuel consumption. Actually the shaft kiln would to-day be entirely superseded by the rotary kiln, and—like the ring or Dietsch kiln—possess only an historical interest for the industry, had it not proved possible, by the introduction of mechanical feed and discharge, to convert it into a kiln of satisfactory output and low heat consumption.

The finely ground fuel is mixed in predetermined proportions with the raw meal, and the mixture is elevated to the feeding platform. It is here uniformly moistened in a mixing screw and then briquetted. The briquettes pass directly from the press into a feeding appliance in the kiln hood. This is usually a revolving plate, from which a scraper removes the briquettes so that they fall into the kiln. The kiln proper consists of a shaft 30 to 50 ft. high and 8 to 10 ft. in diameter, closed below by the mechanical discharging appliance. In Hauenschild's original patent this consisted of a conical crushing grate on a vertical shaft. This has since been modified in design by the various plant manufacturers in many ways, but without departing from the basic principle. It is unnecessary to consider these various forms in the present work, since they do not affect the heat economy of the kiln. Below the discharge is a collecting hopper, which the clinker must leave via a lock, since the air for combustion is forced through this hopper by means of a high-pressure fan or a blast.

The conditions in the kiln can be followed from the curves given in Fig. 5, which show the gas pressures and the temperatures on the inner surface of the kiln at various points along its length; these curves are taken from Richarz.[8] The temperature curve shows that the maximum temperature is attained only 1.87 metres below the kiln head, so that this represents the position of the clinkering zone. The removal of the carbon dioxide from the raw mix thus proceeds extremely rapidly, and by far the greater part of the length of the shaft is used for cooling the clinker and the simultaneous preheating of the air for combustion, which is blown in below. The gas pressure curve shows the loosening of the clinker just above the discharge; at first the gas pressure only falls off slightly. Above this, the gas meets very densely packed clinker, which causes a great decrease in the air pressure. Still higher, in the clinkering,

[8] Zement, Vol. 15, p. 492, 1926.

calcining, and preheating zones, where the material is again more loosely packed, the gas pressure once more falls off slowly, until finally, in the stack, the pressure is only a few millimetres of water gauge.

In Richarz's experiments the raw meal was composed of limestone and blast-furnace slag, so that 1,000 kg. clinker corresponded to 1,352 kg. raw meal, which contained 800 kg. $CaCO_3$. The theoretical heat requirement was therefore $800 \times 425 - 100{,}000 = 240{,}000$ kcal. per 1,000 kg. clinker. The moist raw meal contained 11 per cent. = 167 kg. water per 1,000 kg. clinker. The heat consumption was about 895,000 kcal., and the exit gas temperature about 500 deg. C. Combustion proceeded under almost theoretical conditions, *i.e.*, $\lambda = 1.0$.

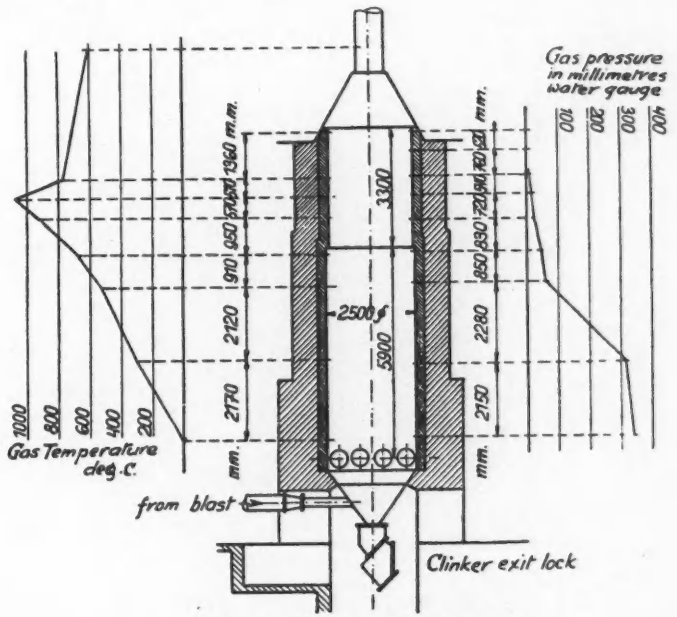


Fig. 5.—Mechanical Shaft Kiln.

The height of the kiln was too small, and the clinker was insufficiently cooled; it must have left the kiln at a temperature of 550 deg. C. The following heat balance can now be derived:—

	kcal.
Theoretical heat requirement	240,000
Evaporation of 167 kg. water (167 × 595)	99,400
Superheating 167 kg. steam to 500 deg. C. (167 × 237) ..	39,600
Heat content of 352 kg. CO_2 at 500 deg. C.	41,700
Heat content of combustion gases from 895,000/7,500 = 119 kg. coal at 500 deg. C., taking $\lambda = 1$ (119 × 162 × 8.96)	172,700
Heat content of 1,000 kg. clinker at 550 deg. C., taking Hartner's value 0.225 for the sp. ht.	123,750
Radiation, conduction, etc., by difference	177,850
Total heat consumption per 1,000 kg. clinker	895,000

The fuel used in these experiments was coke slack of calorific value 6,000 kcal. per kg., which was ground together with the raw materials and was thus very fine and uniformly distributed. The raw-material briquettes could be handled very conveniently, and the kiln was fed by hand. To these circumstances must be attributed the fact that an output of 104,000 kg. clinker per 24 hours could be attained without injecting the air for combustion at an excessively high pressure.

The mechanical feeding of the shaft kiln is a difficult problem. All manner of different constructions have been applied in the endeavour to distribute the raw material uniformly over the whole cross-section of the kiln. Up to the present, however, we have been compelled to content ourselves with distributing the briquettes uniformly around the periphery of the shaft, assuming that the material makes its own way towards the centre. This inward motion actually takes place, but under conditions which are very unfavourable to a material which is readily broken up. The gradual disintegration of the briquettes is unavoidable, and especially so when the raw material lacks plasticity.

The construction of the automatic discharge mechanism aims at breaking away the clinker uniformly from the entire cross-section and removing it from the kiln. The contents of the kiln should thus uniformly sink, and it should be possible, without great difficulty, to maintain the clinkering zone in the position most advantageous for the clinkering reaction and for the adequate cooling of the clinker. In practice, however, the matter is not so simple. In part this is due to the difficulty of uniformly charging the kiln. The irregular distribution and breaking-up of the briquettes fed to the periphery cannot be avoided. This results in the formation of more fine material in certain parts of the kiln than in others, and the resistance to the passage of air and gases varies. On the other hand, the caking of the clinkered material on the kiln walls militates against the uniform downward passage of the kiln contents. The formation of a deposit on one side only of the kiln is particularly undesirable, since this results in the various zones no longer remaining horizontal, and under-burnt, well-burnt, and over-burnt materials are mixed together.

Caking of the material is prevented by: (1) The utmost possible uniform distribution of the fuel, best attained by grinding with the raw materials. (2) Increasing the output as much as possible in relation to the cross-sectional area of the kiln. (3) Artificially cooling the inner surface of the kiln lining.

Grinding the fuel with the raw materials gives uniform distribution not only of the fuel but also of the fuel ash, while the evolution of heat is uniform over the entire kiln cross-section. The ash is, however, chemically absorbed by the clinker, but the effect of this on the quality of the clinker can be corrected by suitable additions to the raw materials.

The reduction in the danger of adherence to the kiln walls attained by increasing the output is obviously due to the increased speed with which the clinkering mass passes down along the walls. The increased output necessitates an increase in the quantity of air blown into the kiln in unit time, and this means higher air pressure and higher power consumption.

The internal surface of the kiln lining can be cooled artificially in two ways: (*a*) By arranging for a hollow space between the refractory lining and the outer shell, through which the air for combustion is blown or drawn before being used in the burning process. (*b*) By replacing the outer insulating layer of brickwork by a sheet-metal shell in immediate contact with the refractory lining. If this is inadequate, the shell can be water-cooled, either entirely or in the critical zone only, in the way that has long been common in blast-

furnace practice. Naturally, this means of artificially cooling the lining increases the heat consumption of the plant.

Consider now Richarz's results for clinkering a normal Portland cement raw mix, making the following assumptions: (1) With a height of shaft at least 40 ft. between kiln hood and discharge, the temperature of the exit gases and of the clinker leaving the kiln is not higher than 400 deg. C. (2) The water content of the moist raw meal is 12 per cent. (3) The losses by radiation, conduction, etc., employing artificial cooling of the lining as in (*b*), are not greater than 250,000 kcal. per 1,000 kg. clinker. (4) In order to exclude the possibility of CO formation, burning is carried out with 10 per cent. excess air, or $\lambda = 1.1$.

The following results are so obtained:

	kcal.
Theoretical heat requirement	420,000
Evaporation of 212 kg. water (212 × 595)	126,150
Superheating 212 kg. steam to 400 deg. C. (212 × 188)	39,850
Heat content of 550 kg. CO_2 at 400 deg. C.	50,900
Heat content of 1,000 kg. clinker at 400 deg. C., taking Hartner's value 0.215 for the sp. ht.	86,000
Radiation, convection, etc.	250,000
Total	972,900

Let the fuel consumption per 1,000 kg. clinker be x kg. of calorific value 7,500 kcal., *i.e.*, 7,500 x kcal. With $\lambda = 1.1$ the heat loss in the exit gases is $128.6 \times 9.82 \times x = 1{,}263x$ kcal. Thus $(7{,}500 - 1{,}263)x = 6{,}237x$ kcal. are utilised in the kiln. Therefore,

$x = 972{,}900/6{,}237 = 155$ kg. fuel = 1,160,000 kcal. per 1,000 kg. clinker.

In practice the heat requirement of the automatic shaft kiln is between 1,100,000 and 1,200,000 kcal. per 1,000 kg. clinker, which agrees very well with the above statement. The output of an automatic shaft kiln of 8 ft. 6 in. internal diameter and 40 ft. height above the discharge can be taken as 75 to 80 tons clinker per 24 hours. Admittedly, a 24-hour output of 100 tons or more is attainable, but can hardly be maintained over long periods if a high degree of uniformity in the quality of the clinker is aimed at. In any case, the means which render possible the present-day increased output of the automatic shaft kiln necessitate increased heat and power consumption.

The Kiln Commission[9] of the Association of German Portland Cement Manufacturers have reported on a 36-hours' test of an automatic shaft kiln of 8 ft. 6 in. internal diameter and 40 ft. shaft height. The shaft was provided with a sheet-metal shell and cooling air was passed between this and the lining. Initially, the air for combustion was blown through this space and thence into the kiln. This, however, proved unsatisfactory, and the air used for cooling was consequently run to waste, while the air for combustion was introduced separately from below the discharge mechanism. Adhesion of the clinkering mass to the sides of the kiln could be prevented by varying the amount of air used for cooling. The kiln was run at a very low output, only 47.5 tons of clinker per 24 hours. It was charged periodically and was thus not completely automatic. Using a powdered coal of calorific value 7,134 kcal. per kg., 11.79 per cent. volatile matter, and 17.9 per cent. ash, the heat consumption was about 1,200,000 kcal. per 1,000 kg. clinker (2,160,000 B.T.U. per 1,000 lb.).

A serious shortcoming of the shaft kiln, which cannot be overcome even in the automatic kiln, is that the results of the burning can only be seen after several hours' running. The valuable information to be obtained from the

[9] E. Schott, Zement, Vol. 15, p. 881, 1926; Vol. 17, p. 1198, 1928.

appearance of the clinker comes much too late to be of service, and, indeed, not before entirely different conditions may be prevailing in the clinkering zone from those represented by the sample under examination. The material in the shaft cannot, at the important stage, be seen or sampled, nor can it be reached by measuring instruments.

B.—The Rotary Kiln.

After the European War the cement industry believed it had found the solution of the fuel problem in the automatic shaft kiln, but was soon compelled to realise that this kiln was unable to cope with the demand for cement of higher quality. The industry was therefore compelled to revert to the rotary kiln, and either reduce its fuel consumption by constructional improvements or utilise the unavoidable waste heat.

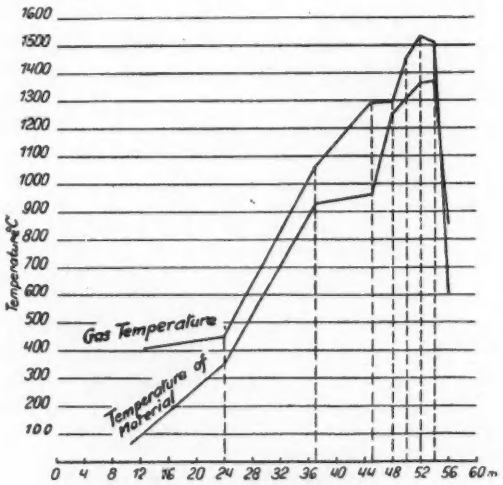


Fig. 6.—Nacken's Diagram.

The reactions inside the rotary kiln are best explained by Nacken's[10] diagram. He made temperature measurements along a 60 m. wet process kiln in normal service, the results of which are shown in Fig. 6.

It will be seen from this figure that after the water of the slurry is evaporated the temperature of the material rises to about 950 deg. C., when a vigorous evolution of CO_2 begins. In spite of the fact that the material passes into a zone of higher gas temperature, its own temperature only very slightly increases during the evolution of CO_2. The exothermic reaction of "fire shrinkage" follows immediately after calcination: the temperature of the material rapidly rises, while the gas temperature, on the other hand, is only slightly reduced, indicating that fire shrinkage proceeds with sufficient evolution of heat greatly to increase the temperature of the material without external heating. There next follows a further heating of the material, but this time accompanied by considerable reduction of the gas temperature. The material then passes the

[10] Nacken and Schoppe, Zement, Vol. 10, p. 581, 1921.

point of maximum gas temperature and immediately begins to cool rapidly, giving up its heat to the secondary air coming from the cooler. It finally passes into the cooler at 900 to 1,000 deg. C.

It should be pointed out that to make temperature measurements on a rotating kiln is an extremely difficult matter, and these results, both for the material and the gases, are certainly too low, particularly in the higher range of temperatures. The highest temperature must actually have been in the neighbourhood of 1,450-1,500 deg. C. for the material and 1,650-1,700 deg. for the gases. Nevertheless, the practical value of Nacken's diagram is in no way diminished by this circumstance.

The most obvious means of improving the heat economy of the rotary kiln is to limit the air used for combustion to the smallest practicable amount. By this is understood the quantity sufficient for complete combustion without CO formation. It is not to be recommended that λ should be reduced below 1.2, *i.e.*, that the oxygen content of the exit gases should be less than 3 per cent., since below this value the saving arising from diminishing the air supply may be several times offset by CO formation.

It is further necessary to draw as much of the secondary air as possible through the clinker cooler, *i.e.*, to avoid the introduction of additional air at the junction

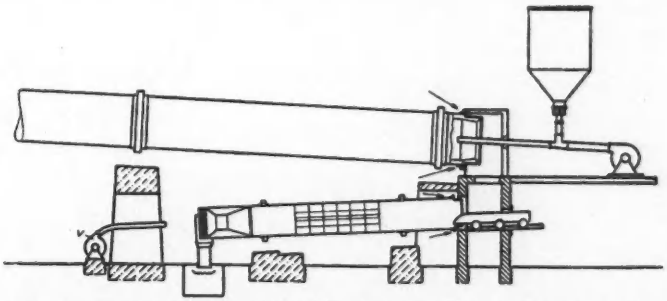


Fig. 7.—Forced Introduction of Secondary Air to the Rotary Kiln.

of kiln and cooler. It is only thus that practically perfect cooling of the clinker can be obtained, and the maximum quantity of the heat of the clinker recovered and used in the kiln. For this reason, all firms of rotary kiln constructors make a great point of providing good seals at the kiln mouth and at the head of the cooler. This is a difficult constructional problem, and an efficient air-tight seal for a tube of 11 ft. 6 in. diameter can only be attained at the cost of increased power consumption, since all stuffing-box constructions exert a strong braking effect, and give rise to other difficulties by reason of the high temperature of the metal employed. Fig. 7 demonstrates an interesting experiment in which the secondary air is forced into the rotary kiln by means of a fan at the exit end of the cooler, instead of relying on the injector action of the coal-firing nozzle or of the stack. In this method the exit end of the cooler is constricted like an injector tube. The fan only delivers part of the secondary air, and the remainder is drawn in by the injector action. Very sensitive air control is thus obtained, and the air pressure can be so regulated as to be $\pm$ 0 mm. water gauge at the seals (see arrows in Fig. 7), so that the construction at these points can be relatively simple. It must be admitted that many raw meals give a dusty clinker, and

that the dust is taken up by the blast from the fan and returned to the kiln, impeding the view of the burner.

It need hardly be stated that the most varied internal constructions have been proposed for improving the heat exchange inside the cooler, and that a fair degree of success has been attained by these means.

In the "Solo" kiln an entirely new idea has been introduced by uniting the kiln and cooler in a single cylinder. In numerous constructions the kiln is lengthened, and the undoubted success of this has resulted in the original idea having been departed from in various ways and developed into new constructive forms.

Attempts have been directed to improving the heat exchange between the gases and the material in the kiln itself. The chief of these consists in widening the kiln in the zones where calcining and clinkering take place, resulting in the form shown in Fig. 8. The effect of this in spreading out the temperature curve is indicated by the Nacken diagram above the figure. The widening of the kiln causes the gas velocity to be diminished, while the exposed surface of the material and the surrounding inner surface of the kiln, which acts as a radiating vault, are increased. In addition, the secondary air is longer in contact with the fuel, and the flame is shortened and the combustion improved.

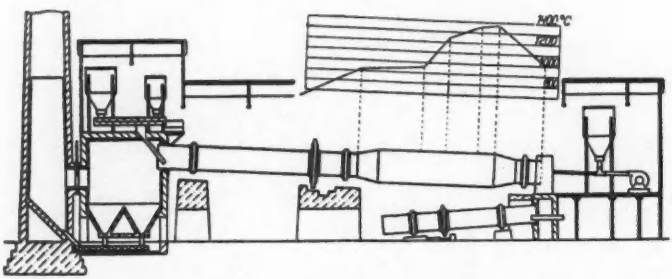


Fig. 8.—Rotary Kiln with enlarged Clinkering and Calcining Zones.

Fire shrinkage is an exothermic reaction, and as soon as the CO_2 is expelled its onset cannot be prevented. A sharp division between calcining and clinkering is thus not possible. It follows that the idea of carrying out calcining alone in a much widened part of the kiln, and then clinkering in a narrow zone with more rapid passage of the material, can hardly be considered to be of practical importance.

It may be pointed out that a good gas seal between the kiln and the smoke chamber is also a matter of importance, especially when the heat in the waste gases is to be recovered.

At first sight it must appear a simple matter to determine the heat distribution in the rotary kiln under different working conditions by practical experiment. The following quantities are obtained from the equations derived earlier in this work:—

(1) xVJ_1 is the quantity of heat used to form 1,000 kg. clinker. If the quantities of clinker and coal are weighed throughout a test and the calorific value of the coal is determined, the calculation of xVJ_1 offers no difficulty.

(2) The theoretical heat requirement of clinker burning may be considered to be known or calculable.

(3) The quantities of CO_2 and steam evolved by the raw meal or slurry can be easily calculated. In the function xVJ_2 the value of V can be calculated from the coal analysis (or with sufficient accuracy from the formula of Rosin). In order to calculate the sum

$$xVJ_2 + 1550\left(\frac{b}{100 - b}\right)(595 + W) + c,$$

which represents the heat content of the kiln exit gases, the only additional requirement is to measure the temperature of the gases across the gas-exit section of the kiln.

(4) The quantity $75x_a$, which represents the total losses excluding those of the kiln-exit gases, can be readily calculated as the difference between quantities (1) and (3).

In connection with (3) we are confronted with the great difficulty of making temperature measurements. It has only recently been realised that the ordinary

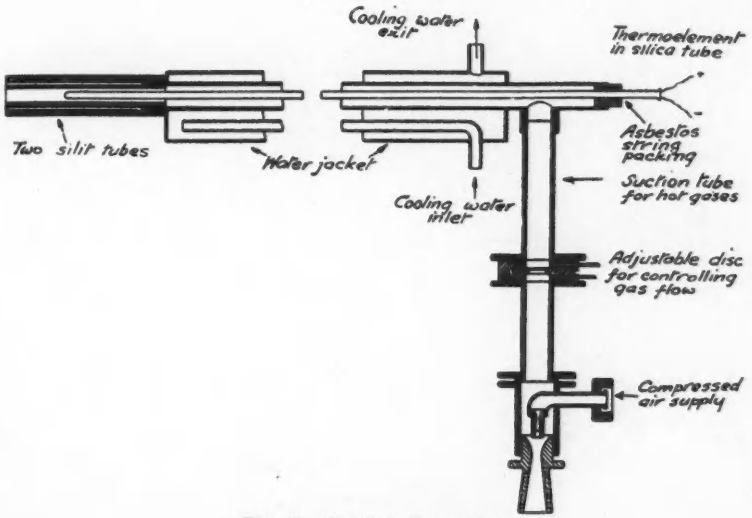


Fig. 9.—Suction Pyrometer.

pyrometer is subject to serious errors in high-temperature gas streams. An important quotation from Paper No. 51 of the Düsseldorf Heat Bureau may here be given: "Thermoelements only give correct readings in gases when the surrounding surfaces are at the same temperature as the gas whose temperature is to be measured. If the gas temperature is different from that of the surrounding surfaces, the true gas temperature is never indicated by the thermoelement, but a temperature between that of the gas and that of the surrounding surfaces is obtained. The error is absolute, and is relatively greater the higher the temperatures involved and the higher the temperature difference between gas and surroundings. The reason for this is that the thermoelement is subject to heat exchange not only with the gases, but also with the radiating surfaces. If heat exchange took place with the gas alone, the gas temperature

would be given accurately. If the gas is at a higher temperature than the surrounding surfaces, the thermoelement will also strive to take up a higher temperature than these surfaces. It then immediately begins to radiate heat to the walls and its temperature sinks until the absorption of heat from the gas by convection is equal to the heat radiated to the walls." These conditions of measurement are present in the highest degree in the case of the rotary kiln. A thermoelement in the kiln lies in proximity to walls whose temperature is much lower than the true gas temperature, and it is to be expected that under certain circumstances errors of several hundred degrees may be made. When it is further pointed out that thermoelements are frequently wrongly constructed, that the pyrometer tubes used are often too short, and that on the other hand long thermoelement leads also cause low results, it will be readily understood that the determined values of the total losses, α—of which the radiation, conduction, and convection losses from the kiln, together with the heat retained by the clinker, form the main part—are often widely different from the true value.

Thus temperature measurements sufficiently accurate for use in the heat balance cannot be carried out with ordinary pyrometers. Only the so-called suction pyrometer (Fig. 9) is suitable for the purpose.

The thermoelement, with its heavy leads, is contained in a fused silica tube. At the hot junction it is surrounded by two silit tubes which are joined on to an iron tube. To enable temperature measurements to be made all over the cross-section of the kiln the instrument must be very long, so that the iron tube must be cooled by water flowing through an annular space. The sucking of the hot kiln gases through the inner silit tube and the attached iron tube can be brought about by means of a compressed-air injector, and the quantity of gas passing through can be controlled by an adjustable disc in the tube. With a silit tube 40 cm. long a suitable diameter for the outer tube is 6 cm. The remaining dimensions of the instrument can be easily derived.

(To be continued.)

Cement in Siam.

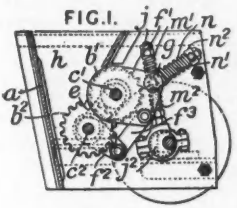
WITH the growing demand for Portland cement in Siam, a factory was erected in Bangkok some years ago by the Siam Cement Co., Ltd., a Siamese concern with European experts. In 1928 and 1930 the plant was modernised by the installation of up-to-date machinery. In 1926 Siam's total consumption of cement was 250,000 barrels, while to-day it is 450,000 barrels a year. The steady increase in demand has also been reflected in imports. There is no special protection in the way of tariffs, the import duty on cement being the same as on most other goods, namely, 5 per cent. ad valorem. Imports of cement into Siam during recent years were as follows:

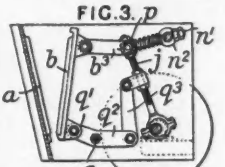
From:	1928/9 Kg.	1929/30 Kg.
Singapore	583,608	104,823
Japan	2,159,093	5,464,314
United Kingdom	120,208	59,192
Indo-China	—	1,761,000
Denmark	6,403,940	5,782,535
Penang	2,865,849	2,760,326
Total (including others)	12,185,510	15,946,889

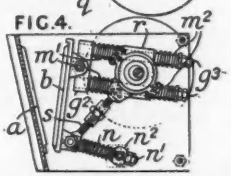
Recent Patents Relating to Cement.

Grinding, Crushing, etc., Mills. MARTINEZ, H. and KIRK, R. H., 4, Stephendale Terrace, St. Peters, Newcastle-on-Tyne. May 21, 1929. No. 333,642.

The operative member or members and/or the abutment opposed to it or them are so mounted that, in the event of choking or fouling, abnormal resistance is absorbed by one or more springs, or other resilient devices are characterised in that the resilient devices are positioned so as to allow the operative member or members and/or the abutment to yield at both the intake and the output end of the machine. The moving jaw comprises two rollers (b^1, b^2), Fig. 1, mounted on shafts (c^1, c^2), of which (c^2) is resiliently mounted and (c^1) is carried by arms (e) movable about the axis of the shaft







GRINDING, CRUSHING, &C., MILLS.

(c^2). The shafts are fixed to levers (f^1, f^2) which are connected together by links (f^3) and the levers (f^1) are provided with perforated crossheads (g) through which slide eccentric rods (j) operated by eccentrics (j^2). The crosshead (g) is maintained in position by springs (m^1, m^2) and a third spring (n) encircles a rod (n^1) connected to the crosshead at one end and slidable in a pivoted block (n^2) at the other. Rotation of the eccentric (j^2) moves the roller (b^1) toward and away from a fixed jaw (a) and so breaks the material entering a hopper (h). If the machine becomes choked the rollers move rearwardly either at the upper or lower end or both, the movement of the eccentric merely compressing the springs (m^1, m^2) alternately. The rollers may be separated and a corrugated, etc., jaw disposed between them. The springs absorbing abnormal resistance to the operative jaw (b) may be dispensed with and the stationary jaw (a) mounted resiliently, or the abutment (a) may be replaced by a jaw operated in the same manner as the jaw (b). In Fig. 3 the moving jaw (b) is connected at the upper end to the eccentric rod (j) by a link (b^3) and at the lower end to a link (q^1, q^2) pivoted at (q), the arm (q^2) being connected by a link (q^3) to the eccentric rod. A rod (n^1) is connected to the eccentric rod by a crosshead (p) and is slidable through a pivoted crosshead (n^2). The link (q^1, q^2) may be resiliently connected at the ends or the pivot (q) may be resiliently mounted. The pivot (q) and crosshead (n^2) may be adjustable to vary the position of the moving jaw (b). The rod (n^1) and crosshead (n^2) may be dispensed with by connecting the eccentric rod to one arm of a pivoted bell-crank lever and permitting the link (b^3) to slide through the other arm against the compression of a spring surrounding the link. In Fig. 4 the sheave (r) of the eccentric (j^2) is bored to receive slidable rods (g^3) connected together and to the moving jaw (b) by a crosshead (g^2). Springs (m^1, m^2) are placed on the rods on each side of the sheave (r) and position the upper end of the jaw (b), the lower end of the jaw being connected by a rod (n^1) slidable against the compression of a spring (n) in a pivoted crosshead (n^2). An adjustable rod (s) may connect the sheave (r) and the lower end of the jaw.

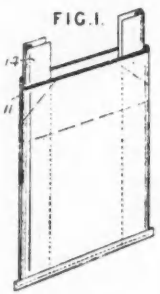
Cements. JACKSON, L. MELLERSH-, 28, Southampton Buildings, London.—(Krupp Grusonwerk Akt.-Ges., F.; Buckau, Magdeburg, Germany.) Sept. 3, 1930. No. 351,328.

In apparatus for concentrating raw cement slurry by hot exhaust gases from the cement kilns, in which the wet slurry in a container (2) is lifted in film form into contact with the hot gases passing along a conduit (1) by rotating discs (4) having scrapers (5), a discharge apparatus comprising a trough (6) and a conveyer worm (8) is provided independent of the container (2). The discs also retain the dust contained

in the gases. The slurry is preferably filtered before being concentrated.

Paper Bags. RAWLINS, J. D., Syston Court, Mangotsfield, near Bristol, and PAPER SACKS, LTD., Keynsham, Somerset. August 14th, 1929. No. 338,170.

A multi-ply bag having a valve opening in one corner is provided with a valve-forming extension comprising an inserted



PAPER SACKS.

strip of material extending down to the lower end of the bag. A single-ply strip of material (14) is folded to fit snugly the gusset (11) of a bag, its lower end reaching to the bottom of the bag and its upper end extending above the top edge thereof. The valve is formed in the usual manner and the strip secured by the sewing at the top and bottom of the bag. An insertion is used at each side of the bag and the flaps of the valves so formed overlap about the longitudinal axis of the bag, one valve serving for filling the bag and the other as an air vent.

Cements. GODDARD, J. F., and SUPER CEMENT, LTD., 10, Upper Woburn Place, London. March 12th, 1930. No. 350,538.

In the dry grinding of cement clinker, gypsum powder, etc., the material to be ground has mixed therewith a segregating agent capable of imparting a dispersive propensity to the pulverised particles being ground. The segregating agent comprises material which when rubbed against the particles being ground generates static electric charges in the particles which induces mutual repulsion; for cement and cement clinker the segregating material is resin or a resinous material. The segregating material may be used alone or with a diffusing material such as plaster of Paris or hydraulic cement, the pulverised resin being mixed with the diffusing material together with a sufficient quantity of water to set the mixture. In the manufacture of cement, one part of resin to five parts of plaster of Paris or hydraulic cement may be used, and one part of this mixture is placed in the mill with each two hundred parts of cement. The segregating and diffusing material is less resistant to abrasion than the material being ground.

Recent Patent Applications.

No. 313,577. NAAMLOOZE VENNOOTSCHAP NEDERLANDSCHE FABRIEK VAN BETON-EMAILLEE FORTOLIET. Method of producing a cement containing cold glaze.

No. 332,322. F. S. WATT. Manufacture of cement.

No. 335,086. BABCOCK & WILCOX, LTD. (Fuller Lehigh Co.). Heat-conducting cement compositions.

No. 336,860. E. L. GEORGE (S.A.I.G.) (SOC. ANON. INVENZIONI GUADAGUIN). Waterproof cements.

No. 354,502. J. F. GODDARD, AND SUPER-CEMENT, LTD.—Manufacture of cement.

No. 355,564. METALLGES. AKT.-GES.—Process for sintering and calcining cement.

No. 355,583. H. E. POTTS (Chemische Fabrik Grunau Landshoff and Meyer Akt.-Ges.).—Process for making cement impervious.

No. 355,678. E. BOYNEBURG.—Producing magnesian Portland cements.

No. 356,144. DR. K. BIEHL.—Hydraulic cements.

No. 356,611. MIAG MUHLENBAU UND INDUSTRIE AKT.-GES.—Process and apparatus for manufacturing cement.

Estimation of Free Lime in Cement.

By Dr. G. A. ASHKENASI.

(CHIEF CHEMIST, THE PORTLAND CEMENT CO. "NESHER," LTD., PALESTINE.)

THE estimation of free lime has always been an important problem in cement research. The analytical chemist has tried by detection of free and combined lime to investigate the constitution of Portland cement, and the works chemist has to eliminate free lime by controlling the burning process. From Sainte Claire Deville[1], who tried to estimate free lime by means of a solution of ammonium nitrate in absolute alcohol, till to-day many reports have been published on methods of solving this problem. In 1909 Professor Alfred D. White[2] found a solution to the qualitative detection of free lime, based on the formation of crystalline calcium phenolate which can be readily recognised in the polarised light of the microscope. D. C. McFarland and H. F. Hadley[3] recommended the use of p. cresol instead of phenol, and their method is more exact and defined.

The main drawback to the quantitative estimation was that cement when mixed with water-containing agents was hydrolysed; by using other means, part of the combined lime was also attacked. The idea of Maynard[4], to extract calcium oxide from cement by means of glycerol, was developed by W. E. Emley[5], who found a method for detecting the quantity of free lime in cement. Emley's method, now used in cement practice, is based on the extraction of uncombined calcium oxide with alcoholic solution of glycerol and titration of the calcium glycerate with an alcoholic solution of ammonium acetate. This method is, however, rather complicated. It needs much time and very great care in the preparation of reagents, which must be absolutely free from water. It is especially difficult to make ammonium acetate water-free. Further sources of error are special conditions of the titration, the separation of ammonia by heating under a reflux condenser, and long-continued heating which causes a precipitate of crystalline calcium glycerate, rendering the titration less accurate. The author has for several months examined this method in the works laboratory and has always obtained varying results.

Others, also, have obtained unreliable results. Lerch and Bogue[6] gave out for examination eight different cements to seventeen laboratories, and the results varied by about 25 per cent. Sample N_1, for instance, showed as maximum a proportion of 8.5 per cent.; as minimum 6.3 per cent.; sample N_8 showed as maximum, 7.8 per cent.; as minimum, 5.7 per cent. When one examines commercial cement, which is usually partly hydrolysed, the results obtained by Emley's method are quite unacceptable. Therefore attempts were made to replace the ammonium acetate by another reagent.

Dr. Eng. H. Rathke[7] found a more suitable one in tartaric acid, and G. E. Bessey[8] used benzoic acid with success. Titration by these reagents is more simple and the results obtained are concordant. In order to obtain the N/10

[1] Sainte Claire Deville. "Journ. für prakt. Chemie," pp. 62, 81.
[2] A. White. "Ind. and Eng. Chem.," No. 1, 1909, p. 5.
[3] McFarland and H. F. Hadley. "Chem. Zeit.," No. 122, 1912.
[4] Maynard. "Tonind. Zeit.," No. 27, 1903, p. 1253.
[5] W. E. Emley. "Trans. of Am. Cer. Soc.," No. 17, 1915.
[6] Lerch and Bogue. "Zement," 1931, p. 653.
[7] H. Rathke. "Tonind. Zeit.," 1928, p. 1318; "Zement," 1931, No. 28.
[8] G. E. Bessey. "Journ. of Soc. of Chem. Ind.," 1930, p. 360.

tartaric acid, Dr. Rathke suggests heating pure calcium oxide with anhydrous glycerol for twenty-four hours at a temperature of 60-70 deg. C., shaking the mixture from time to time. The CaO is completely dissolved by this time. This solution is tested with alcoholic solution of tartaric acid, using phenolphthalein as indicator.

The writer simplified this method, omitting the twenty-four hours' heating and shaking, and acting as follows:

Standardising N/10 Tartaric Acid.—Dissolve 7.5 gr. tartaric acid in 1,000 c.c. absolute methanol. Rub thoroughly 50 mg. purest CaO with 2 c.c. glycerol of 1.26-1.262 sp. gr. in an agate mortar; wash this mixture into an Erlenmeyer flask with 8 c.c. glycerol (four times each with 2 c.c.) and then with 10 c.c. methanol. Then add another 30 c.c. methanol, cover the flask with a watch-glass, and boil. The muddy liquid becomes clear after boiling for three or four minutes. Longer heating is to be avoided to prevent the precipitation of crystalline calcium glycerate. The boiling solution is tested with the prepared N/10 solution of tartaric acid, using methyl alcohol solution of phenolphthalein as indicator. The titration takes place readily, the change of the colour of the indicator from red-rose to colourless is sharp, and the difference between the results obtained does not exceed 0.1 c.c. It must be borne in mind that one always obtains a higher amount of CaO. Instead of the theoretical value of 0.0028 gr. CaO corresponding to 1 c.c. of N/10 tartaric acid, an average of 0.0036 gr. is obtained. The same value is obtained by using calcium hydroxide instead of calcium oxide. For neutralisation, 66 mg. $Ca(OH)_2$ need 13.7 cc. N/10 tartaric acid (average), which equals 0.00364 gr. CaO to 1 c.c. N/10 tartaric acid.

G. E. Bessey[9] by titration with benzoic acid has also obtained higher results, which vary in his tests between 0.0030 and 0.0037 gr. CaO=1 c.c. N/10 $C_6H_5CO_2H$. Bessey explained this divergence by the hydrolysis of the compounds of calcium glycerate, or by the formation of small quantities of stable compounds with remainders of acids, which are produced by heating the glycerol. No plain explanation can be given here of this difference between the theoretical and empirical values, but as this divergence in numerous tests was always the same the empirically fixed value is adhered to and all tests are based on the resulting equivalent: 0.0036 gr. CaO corresponds to 1 c.c. of the author's $C_4H_6O_6$ solution. For tests the writer used cement made in the Haifa factory by the dry process in rotary-grate shaft-kilns. A great number of various samples were examined, but it is sufficient to describe here three typical cases.

Cement A made of well-burnt, completely sintered clinker, ground without gypsum in the laboratory mill to a fineness of no residue on the 180² sieve.

Cement B made of underburnt clinker, ground in the same way without gypsum and to the same fineness.

Cement C was an average sample of works grinding in compound mills. The clinker was ground with 2.5 per cent. gypsum to a fineness of 3.4 per cent. on the 180² sieve. This cement, tested for soundness by the Le Chatelier method, showed an expansion of 1 mm. after twenty-four hours' aeration; tested for tensile strength according to the B.S.S., it gave, after three days, 485 lb. per sq. in.; after seven days, 559 lb. per sq. in.; after twenty-eight days, 607 lb. per sq. in.

Before being titrated the cement was either dried at 120 deg. C., or heated until constancy of weight in an electric muffle furnace at 1,050 deg. C. was

[9] G. E. Bessey, "Zement," 1931, p. 654.

obtained. One gramme of cement so treated was rubbed with 2 c.c. of glycerol in an agate mortar, washed with glycerol (four times with 2 c.c.) and then with 10 c.c. methanol into an Erlenmeyer flask and another 30 c.c. methanol added. The flask was covered with a watch-glass and the mixture boiled for three to four minutes and immediately titrated, using a 0.5 per cent. solution of phenolphthalein in methanol as indicator. Titration was continued until the red and later rose colour of the liquid disappeared. This change is very clear. In the samples which were only dried at 120 deg. C. the rose colour returned after several minutes and disappeared on the addition of one drop of tartaric acid, and then after one minute it again returned. In the samples which were ignited, the change of colour of the indicator was maintained during several hours, even when the flask was covered with a watch-glass.

When one continues titration with samples which have only been dried in order to stop recurrences of the rose colour, a point is reached where the liquid remains colourless for hours. Thus, for example, in titrating cement C, 3 c.c. of N/10 $C_4H_6O_6$ were needed to obtain the first change. It was necessary to add another 3.8 c.c. of acid to obtain a lasting change. This phenomenon can be explained by the presence of basic calcium compounds which react slowly. In the ignited cement the change lasts several hours, and when the flask is firmly closed the liquid remains colourless for several days. In this case the change to rose colour is caused by the presence of traces of water, which are unavoidable and even necessary for the action of the indicator.

In Table 1 typical results of the estimation of CaO in dried and ignited cement are given. These tests were carried out by Dr. N. Ben-Jacob, assistant to the author.

TABLE I.

(Percentage CaO shown by the glycerol-tartaric acid method of testing cement.)

	Samples dried at 120° C.		Samples ignited at 1,050° C.	
	No. of c.c. of N/10 Tartaric Acid.	% of CaO.	No. of c.c. of N/10 Tartaric Acid.	% of CaO.
Cement A ..	2.3 ; 2.25 ; 2.35	0.83	2.4 ; 2.35 ; 2.4	0.85
Cement B ..	26.3 ; 26.2 ; 26.35	8.43	29.9 ; 29.8 ; 29.8	10.53
Cement C ..	3.0 ; 2.9 ; 3.05	1.27	35.7 ; 35.8 ; 35.65	12.93

The results obtained show that the proportion of CaO detected in the well-sintered clinker is the same, independent of the treatment before the detection. In underburnt cement the proportion of CaO increases when the cement has been ignited. The increase amounts in the case of cement B to 2.10 per cent., caused by the presence of calcium carbonate. (This cannot be estimated by this method in cements which have only been dried.) When ignited, $CaCO_3$ forms CaO and increases the amount of free lime.

Cement C, containing gypsum, yields widely different results. The proportion of CaO, which in the dried samples equals 1.27 per cent., increases in the ignited to 12.93 per cent. The volatile matter evolved by the ignition of cement C was tested; it was composed of 1.47 per cent. carbon dioxide and of 2.34 per cent. steam. Sulphuric anhydride or sulphur dioxide was not found. The amount of carbon dioxide evolved justified an increase of 1.89 per cent. calcium oxide, but the results obtained showed an increase of 11.66 per cent.

To investigate this phenomenon further, samples of cement C were ignited for three, four, twenty-four, and thirty hours. Constancy of weight was obtained after about two hours' ignition. The results of titration of cement after various periods of ignition at 1,050 deg. are as in Table II.

TABLE II.

	No. of c.c. of N/10 $C_4H_6O_6$.	Average % CaO.
Cement heated at 1,050° C. for 3 hours	36.35 ; 36.45	13.18
,, ,, ,, 6 ,,	38.80 ; 38.70	13.97
,, ,, ,, 24 ,,	39.10 ; 39.0	14.06
,, ,, ,, 30 ,,	39.05 ; 38.90	14.03

A small increase was found, which reached the maximum when the samples had been heated for six hours. To examine the influence of the amount of gypsum added, another 1, 2, 3, and 4 per cent. of finest ground gypsum dihydrate were added to cement C, which already contained 2.5 per cent. Some of these samples were dried at 120 deg. C., and some of them heated at 1,050 deg. C. for different periods. The samples were then titrated, with the following results (Table III) :

TABLE III.

(Percentage of estimated CaO in cement C.)

Gypsum added.	Samples Dried at 120°C.	Samples Heated at 1,050 deg. C. During 3 Hours.	4 Hours.	8 Hours.	24 Hours.
1% ..	1.08 ; 1.03	13.53 ; 13.88	—	—	13.80 ; 13.65
2% ..	0.98 ; 0.99	13.82 ; 13.88	—	—	18.61 ; 18.67
3% ..	1.13 ; 1.07	14.32 ; 14.11	16.21 ; 16.30	19.01 ; 18.86	19.06 ; 18.87
4% ..	1.02 ; 1.09	—	—	—	18.90 ; 18.93

The results show that the estimated quantity of CaO in the dried cement is independent of the increase of the amount of gypsum. In the ignited samples, when the proportion of gypsum is greater than 3.5 per cent., the estimated quantity of CaO increases with the increasing amount of gypsum and with the duration of the ignition, but after six or eight hours' heating and with the addition of 2 per cent. of gypsum this increase reaches its maximum. This increase cannot be caused by the decomposition of gypsum, because cement with gypsum ignited at 1,050 deg. C. does not lose sulphuric acid; secondly, the quantities of CaO found were much higher than the amount of CaO in the gypsum used.

It must be accepted that calcium oxide is liberated from cement when cement containing gypsum is heated. This liberation is limited; the amount of free lime is the same when cement contains 4.5, 5.5, or 6.5 per cent. gypsum. In this respect this phenomenon is similar to the action of gypsum as a setting-time retarder. The more probable assumption is that gypsum, when heated with cement, decomposes the loosely combined calcium compounds in cement and makes lime free. Further research on this subject is being undertaken.

The Theory of Cement Formation.

By RUDOLF ZOLLINGER.

CEMENT is a material possessing hydraulic properties which have their origin in the free calcium hydroxide present. This free lime is formed in the cement on the addition of water by the decomposition of silicates and aluminates supersaturated with respect to lime. It is only in the case of such supersaturated compounds that decomposition with the liberation of lime is possible.

Of the compounds of SiO_2 and CaO, the following may be considered supersaturated with CaO:—$3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.2SiO_2$ and $4CaO.3SiO_2$. These four compounds tend to give up CaO and form the stable compound $CaO.SiO_2$. As regards the compounds of Al_2O_3 and CaO, the following must be considered supersaturated with CaO:—$3CaO.Al_2O_3$, $2CaO.Al_2O_3$ and $5CaO.3Al_2O_3$. These tend to split off CaO, forming the stable $CaO.Al_2O_3$. Thus the calcium silicates of cement must be sought in the range $3CaO.SiO_2$—$CaO.SiO_2$, and the calcium aluminates in the range $3CaO.Al_2O_3$—$CaO.Al_2O_3$.

In cement, however, we are neither concerned with pure silicates nor—except in the case of the theoretically purest aluminous cements—with pure aluminates. We are rather dealing with mixed crystals of silicates and aluminates. If the silicates preponderate we have Portland cements, while if the aluminates are in excess we have the so-called aluminous cements. In both cases the cements must be sought in the region of the ternary diagram bounded by the equilibrium lines

$$3CaO.SiO_2 \leftrightarrow 3CaO.Al_2O_3 \text{ and}$$
$$CaO.SiO_2 \leftrightarrow CaO.Al_2O_3$$

This area is shown in Fig. 1. The former of these lines represents the highest attainable degree of supersaturation (*i.e.*, the cement of best hydraulic properties), while the latter represents cements which cannot possess any further hydraulicity since all lime supersaturation has disappeared and the system has assumed its stable form. In the region above the second line the splitting off of lime can only take place with difficulty, *i.e.*, by overcoming great internal resistance. Cements of practical value will only be found in the region occupied by compounds supersaturated with respect to lime, as will be shown later.

Limestone and clay, or substances such as marl which are a natural mixture of these, are the usual raw materials of cement manufacture. The technical process consists of opening up the natural silicates with CaO. The relatively feeble base CaO is sufficient for this purpose since the silicates of clay are supersaturated with silica and readily give up their excess. In cement manufacture we not merely break down the SiO_2-supersaturated silicates of the clay, but further produce a product supersaturated with CaO. Then we make use of this opposite instability by converting the energy of decomposition of the new supersaturated compounds into hydraulicity.

The most varied members of the class of sedimentary rocks are utilised as sources of lime. Among these the mineral calcite, chemically $CaO.CO_2$, is extremely common. This is burnt to drive off the CO_2 (calcination) and obtain the lime in the free state. If the calcite-containing rock occurs in porous form it is known as tuff, lime tuff, or travertine. The dense compact form is limestone, while the earth-like modification is chalk. Coral and marble may also be mentioned, although they are rarely used in cement manufacture on account of their hardness and the consequent high cost of grinding.

While the composition of limestone is always relatively simple, that of clay is complicated. Clay consists of mixed crystals of aluminium silicates with calcium or alkali silicates, the SiO_2 being always combined with at least two bases. In expressing clay in the ternary diagram the alkali or magnesium silicates present must be calculated as calcium silicates, and the ferric silicates, with those of any other metals, as aluminium. This can be justified theoretically, since the action of the alkalis and magnesia in cement is identical with that of lime, while the other metallic oxides have the same effect as alumina. Let us now represent the possible calcium silicates on the SiO_2-CaO ordinate and the aluminium silicates on the SiO_2-Al_2O_3 ordinate as in Fig. 2. Then the lines joining compounds of the same type give the equilibria in the mixed crystals occurring in clay. If these equilibrium lines are intersected by the line $SiO_2 \longleftrightarrow CaO.Al_2O_3$, the points of intersection correspond to the molecular mixed crystals which occur as minerals in nature and of which the degradation product is clay. Naturally there are other mixtures present besides the four representative types shown in Fig. 2.

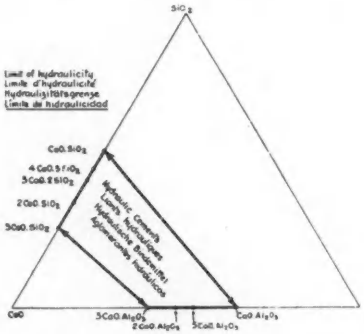


Fig. 1.

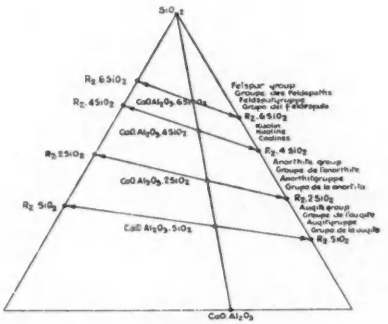


Fig. 2.

These do not affect the picture, however, and would only complicate it. Thus the following four types of minerals must be distinguished and accounted for in our calculations:

(1) $CaO.Al_2O_3.6SiO_2$, the hexasilicates. In clay these are represented by the felspars.

(2) $CaO.Al_2O_3.4SiO_2$, the tetrasilicates. These are the kaolin of clay.

(3) $CaO.Al_2O_3.2SiO_2$, the bisilicates, occurring in clay as the mineral anorthite or lime felspar.

(4) $CaO.Al_2O_3.SiO_2$, the monosilicate. This occurs in nature as the minerals of the augite and hornblende series.

Remembering that the minerals supersaturated with respect to SiO_2 tend to decompose, giving an end product of the formula R_2SiO_2, it can be predicted that the felspars will most readily react, and the augites not at all. If the silica content is higher than that of the hexasilicates we are no longer dealing with mineral compounds. Clay containing such high proportions of silica must be considered as a mixture containing free silica, *i.e.*, sand or quartz. Such clays are not regarded with favour, and in practice they are separated from the free silica by sedimentation. From these facts the following deductions regarding the production of cement may be drawn.

In Fig. 3 the highest and lowest silicates are joined to the CaO point. These new lines represent the equilibria of cement formation, *i.e.*,

$$CaO.Al_2O_3.6SiO_2 + xCaO, \text{ and } CaO.Al_2O_3.SiO_2 + xCaO.$$

These lines intersect the equilibrium lines of the calcium silicates-calcium aluminates system relating to cement, and thus further limit the field of possible cement formation, so that it can be stated that Portland cements can only lie in the area ABCD, and aluminous cements in the area marked out by B,C, $3CaO.Al_2O_3$, $CaO.Al_2O_3$, possibly extending to $CaO.Al_2O_3.SiO_2$.

It is seen from Fig. 4 that the area ABCD is intersected by three further systems. If a cement falls on the line $CaO.SiO_2 \leftrightarrow CaO.Al_2O_3$, it will not possess hydraulic properties, since this line represents mixtures of the two stable components. Thus the first true cement is represented by point I, which represents the equilibrium $2CaO.SiO_2 \leftrightarrow CaO.Al_2O_3$. The equilibrium $CaO.SiO_2 \leftrightarrow 2CaO.Al_2O_3$ can, however, also hold in a cement of this composition, so

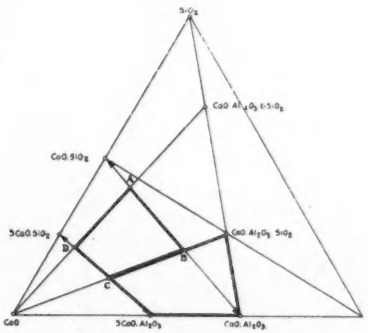


Fig. 3.

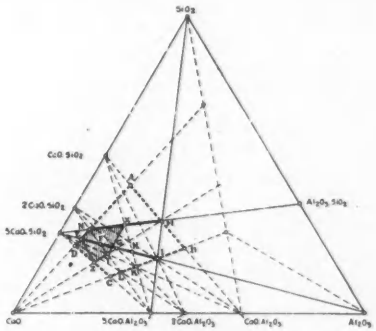


Fig. 4.

that it can be supersaturated with respect to both the calcium silicate and the calcium aluminate component. We are thus concerned with a limiting case, and this cement can be considered as a representative of both the Portland and the aluminous cements; point I is the transition point between the two systems.

In cements corresponding to N and M, aluminium silicates can exist as a third component, along with the equilibrium calcium silicates-calcium aluminates. Thus at N we may have the equilibria

$$5(3CaO.SiO_2) \leftrightarrow (Al_2O_3.SiO_2)$$
$$(3CaO.Al_2O_3) \leftrightarrow 6(2CaO.SiO_2).$$

At M we have

$$(3CaO.SiO_2) \leftrightarrow (Al_2O_3.SiO_2)$$
$$2(CaO.SiO_2) \leftrightarrow (CaO.Al_2O_3).$$

In this neighbourhood lies the transition to glass or slags.

A definite area of equilibrium between calcium silicates and aluminates is outlined by CDEI, or possibly CDNMI. It is only in this area that we are certain of finding Portland cements. Taking the intersections of the equilibrium lines of the system calcium silicates $\leftrightarrow$ calcium aluminates with the lines bounding CDEI, the cements C, D, E, F, G, H, I, K and L are found. The cements C, L, K, I, have, however, no practical importance. It has already been seen

that the line $CaO \leftrightarrow CaO.Al_2O_3.SiO_2$ on which they lie belongs mineralogically to the augite-hornblende series, the minerals of which have attained the stable state and only give up SiO_2 with difficulty. In practice this means that these minerals are difficult and costly to open up, and clays of this composition are not worked. Owing to their theoretical interest, however, they may nevertheless be considered in the present article. The mineralogical character of the above cements may be expressed as follows:

Cement C $(3\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
,, D $6\ (3\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
,, E $3\ (3\ CaO.SiO_2)—(2\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
,, F $3\ (2\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
,, G $2\ (2\ CaO.SiO_2)—(2\ CaO.Al_2O_3)$
,, H $3\ (CaO.SiO_2)—2\ (3\ CaO.Al_2O_3)$
,, I $(2\ CaO.SiO_2)—(CaO.Al_2O_3)$
$(CaO.SiO_2)—(2\ CaO.Al_2O_3)$
,, K $(CaO.SiO_2)—(3\ CaO.Al_2O_3)$
$(2\ CaO.SiO_2)—(2\ CaO.Al_2O_3)$
$(3\ CaO.SiO_2)—(CaO.Al_2O_3)$
,, L $(2\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
$(3\ CaO.SiO_2)—(2\ CaO.Al_2O_3)$

The corresponding chemical compositions are

Cement.	Modulus.	CaO	Al_2O_3.	SiO_2.
C	2.06	67.43	20.48	12.09
D	2.53	71.72	6.24	22.04
E	2.17	68.50	6.94	24.56
F	1.80	64.10	12.96	22.94
G	1.51	60.16	18.27	21.57
H	1.34	56.75	22.99	20.16
I	1.00	50.88	30.90	18.22
K	1.38	57.99	26.42	15.59
L	1.72	63.31	23.07	13.62

All cements falling within the pentagon CDNMI must be considered theoretically possible. The difficulty of opening up minerals of the augite hornblende series, which would be out of all proportion to the value of the resulting cements, prohibits the use of clays containing an excess of these minerals. The raw materials available apart from these are mainly clay containing kaolin or kaolin felspar.

If we insert in the theoretically determined pentagon the extremes of the cements found in practice, we get a smaller pentagon, approximately DNXYZ. The cements corresponding to the apices of this figure may be represented as follows:

Mineralogical.

Cement D $6\ (3\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
,, N $5\ (3\ CaO.SiO_2)—(Al_2O_3.SiO_2)$
$6\ (2\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
,, X $3\ (CaO.SiO_2)—(3\ CaO.Al_2O_3)$
$2\ (3\ CaO.SiO_2)—(Al_2O_3.SiO_2)$
,, Y $2\ (2\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$
$2\ (3\ CaO.SiO_2)—(CaO.Al_2O_3)$
,, Z $2\ (3\ CaO.SiO_2)—(3\ CaO.Al_2O_3)$

Chemical.—Cement.	Modulus.	CaO.	Al_2O_3.	SiO_2.
D	2.53	71.72	6.24	22.04
N	1.80	64.45	7.85	27.70
X	0.98	54.30	16.50	29.20
Y	1.77	63.79	16.61	19.60
Z	2.26	69.43	14.03	16.54

Thermal Dissociation of Ferric Oxide in Cement Burning.

In a recent number of "Zement," Dr. H. Kühl and R. Rasch state: The part played by Fe_2O_3 in the clinkering of cement has not up to the present been satisfactorily elucidated. The dissociation of Fe_2O_3 under the conditions prevailing in the rotary kiln has therefore been investigated. The method consisted of measuring the oxygen evolved by pure Fe_2O_3 and various cement-like mixes on heating under controlled conditions. The material, contained in a platinum boat, occupied a confined space in a gas-tight sillimanite tube, filled originally with oxygen. This was heated to various temperatures for definite periods in a carbon resistance furnace, and the oxygen evolved was measured in a gas burette, making all necessary corrections.

In a preliminary experiment, 3g. of pure Fe_2O_3 were heated between 1,300 and 1,500 deg. C. Traces of gas were evolved below 1,400 deg., and 25 minutes at 1,400 gave 2.2 c.c. oxygen, 20 minutes at 1,450 deg. gave a further 8.1 c.c. gas, and 65 minutes at 1,500 a further 28 c.c., or a total of 38.3 c.c. The theoretical maximum amount of oxygen was 70.1 c.c. The results show that the speed of decomposition of Fe_2O_3 rapidly increases with temperature. It is, however, remarkable that the reaction rapidly comes to a standstill at all the temperatures investigated, although about half the original Fe_2O_3 may be still undecomposed. This is possibly due to the formation of solid solutions of Fe_2O_3 and the Fe_3O_4 to which it gives rise.

In the main experiment the evolution of oxygen at 1,500 deg. (which temperature was attained as rapidly as possible) was studied in the case of raw mixes representing mono- and di-calcium ferrites, $4CaO.Al_2O_3.Fe_2O_3$ (celite), an aluminous cement, a Portland cement, and a blastfurnace slag all rich in Fe_2O_3. The CO_2 was driven from the raw mixes before they were placed in the carbon furnace. With these mixtures the evolution of oxygen was much slower than with pure Fe_2O_3. The slowing up of the reaction with time is again observed, and it would appear that the ferrites are partly dissociated, and that the oxygen is evolved by the Fe_2O_3 which is first formed.

The dissociation curves of these materials can be divided into three groups, characterised by their lime contents. Monocalcium ferrite (i.e., the system lowest in lime) gives relatively rapid evolution of oxygen. A mid position is occupied by dicalcium ferrite, aluminous cement and slag, while Portland cement and celite give up least gas.

In the normal running of the rotary kiln the evolution of oxygen from Fe_2O_3 must be concluded to play only a minor part. It is, however, quite appreciable, and the consequent presence of Fe_3O_4 is the cause of the definite absorption of pot. permanganate shown by most Portland cements. In the case of overburning the formation of a melt may be assisted by the presence of the Fe_3O_4, while a definite portion of the hydraulic factor may be lost from the point of view of combination with CaO; i.e., the lime content of the mix will be too high for the erroneous conditions set up. The greenish-black colour of normal clinker is mainly due to the presence of Fe_3O_4. The brown or red clinker obtained under certain conditions of incorrect burning may be due to a mixture of Fe_2O_3, Fe_3O_4 and calcium-iron compounds—although the formation of reddish clinker is even now not satisfactorily explained.

Fineness and Sieving of Portland Cement.

By A. C. DAVIS, A.M.I.Mech.E., M.Inst.C.E.I., F.C.S.

(WORKS MANAGING DIRECTOR, ASSOCIATED PORTLAND CEMENT MANUFACTURERS, LTD.)

ONE of the first observations the user makes in regard to the quality of a cement concerns its fineness, and the cement is mechanically and subconsciously passed through the fingers in order to feel the size of grain. The coarse particles can thus be readily perceived, and a practised tester is in this way able to gauge approximately the fineness of grinding. The determination of the fineness of Portland cement has some importance because a finely ground cement is sounder and stronger in mortar. The apparatus used and methods adopted in the fineness tests are not very exact, but since strictly precise results are not absolutely essential they are perhaps sufficient for the purpose, although methods of separation by air and fluid are receiving increasing attention as fineness of grinding increases.

The finer grinding of cement does not always increase—in fact, it may appear to reduce—the tensile strength of neat briquettes, but the strength of a mixture of sand and cement is definitely improved by increased fineness. This explains the growing desire for finer cement, and the finer grinding now practised is an improvement in the manufacture greatly in favour of the consumer, both as regards economy in use and reliability of result. Much has been written concerning the value of finely ground cements, but it may be advisable to explain further the results to be expected in testing, and also in using, a finely ground material. Unless the finer cements are competently dealt with and thoroughly understood, the cement user may be prejudiced against what is undoubtedly a superior article, and in some quarters reversion to coarse grinding has been advocated owing to lack of appreciation of the real causes underlying difficulties sometimes experienced, such as crazing.

Years ago cements were made with 10 per cent. or more residue on a 50 × 50 sieve (*i.e.*, 2,500 meshes to the square inch), and good work was done with cements of this fineness, but to-day the residue may be less than 5 per cent. on a British Standard fine sieve No. 170.

The British Standard Specification for Portland cement calls for a cement that shall be ground to comply with the following conditions of fineness:

100 grammes (or, say, 4 oz.) of cement shall be continuously sifted for a period of 15 minutes on a sieve of B.S. Mesh No. 170, and the residue for a period of not less than 5 minutes on a sieve of B.S. Mesh No. 72, with the following results:

"(1) The residue, by weight, on a sieve of B.S. Mesh No. 170 shall not exceed 10 per cent.

"(2) The residue, by weight, on a sieve of B.S. Mesh No. 72 shall not exceed 1 per cent.

"Air-set lumps in the samples may be broken down with the fingers, but nothing shall be rubbed on the sieve.

"The sieves shall be prepared from wire-cloth complying with the requirements of Table I of the British Standard Specification for Test Sieves (B.S.S. No. 410). The wire-cloth shall be woven (not twilled) and carefully mounted on the frames without distortion. The sieving area shall be not less than 50 square inches (322.58 square centimetres) and the depth of the sieves shall be

not less than $2\frac{3}{4}$ inches (69.85 mm.) measured from the surface of the wire-cloth."

The nominal dimensions and tolerances for sieves for testing cements are given in Table I:

TABLE I.

DIMENSIONS OF STANDARD SIEVES FOR TESTING CEMENT.

B.S. Mesh No. (Nominal meshes per lineal inch.)	Nominal size of aperture (side of square).		Nominal diameter of wire.			Approx. screening area.	Tolerance on average aperture, plus or minus.
	in.	mm.	in.	mm.	Standard wire gauge.	Per cent.	Per cent.
170	0.0035	0.089	0.0024	0.061	46	35	8
72	0.0082	0.211	0.0056	0.142	$38\frac{1}{2}$	36	6

The maximum tolerances for occasional large apertures, if present, expressed as percentages of the nominal dimensions for side of aperture in either direction, shall not exceed 50 per cent. for the sieve of B.S. Mesh No. 170, and 35 per cent. for the sieve of B.S. Mesh No. 72. No sieve shall be regarded as Standard which does not conform to these requirements.

Fineness of grinding is very important because the finer the cement the more intimately can it be incorporated into the aggregate used for the concrete and therefore the stronger will be the ultimate work, or if economy is more necessary than increased strength then a leaner mix can be used. At the same time, as already stated, the use of a fine cement necessitates proper understanding of its properties.

The fact has been well established that, other qualities being equal, finer cement has a greater sand or aggregate carrying capacity; that is, it will show an increased strength with the same charge of sand, or equal strength with a greater charge. Tests of neat cement, or extremely rich mortar, obscure this valuable quality. On the other hand, fineness of grinding alone is not to be taken as indicating the quality of a cement, as weakly burned cements will give a larger proportion of fine material for the same amount of grinding than those ground from a harder clinker, though the latter are usually the more valuable cements.

Portland cement as delivered by the manufacturer may be considered as a mixture of coarse and fine particles (respectively known as "residue" and "flour"). The value of cement with a high proportion of "flour" is, first, that the actively cementitious property of the material is principally in the very fine particles, and, second, that the "residue" is practically inert, or at all events hydrates so slowly that it may be regarded as so much aggregate; that is to say, this residue is clinker which has been only partially reduced in the process of grinding, so that the gauging water attacks the surface of the particles and leaves a comparatively large inactive mass in the interior. If these particles were reduced to flour, they would be found to produce a good quality cement showing a high tensile resistance.

The ever-increasing fineness to which cement must be ground to meet modern demands has reached a point where ordinary methods of sifting have to be supplemented by some other method of separating the finer particles into different sizes of grains, and the elutriator or "flourometer" test, described later, is sometimes used.

The proportions of the coarse and fine particles and "flour" in a number of different samples of cement tested for fineness on standard sieves and for flour percentage are shown in Table II:

TABLE II.

Sample No.	Per cent. residue on B.S. Sieve No. 72.	Per cent. residue on B.S. Sieve No. 170.	Per cent. flour in flourometer.
1	Trace	4.80	57.55
2	0.10	5.00	58.45
3	0.25	7.10	54.70
4	0.10	3.30	62.35
5	0.10	3.70	60.40
6	0.05	2.80	67.50
7	0.05	3.80	61.00
8	0.15	5.00	58.15
9	Trace	3.30	58.15
10	0.10	5.20	56.50
11	Trace	0.40	76.05
12	Trace	0.25	75.10
13	Slight Trace	0.40	78.25
14	Trace	0.60	76.50
15	Trace	0.30	77.50
16	Trace	0.50	75.00

From time to time, to show the comparative adhesive and cohesive qualities of fine and coarse Portland cements, cements have been ground to an increasingly greater degree of fineness. Tensile tests made with standard mortar from these cements show the higher results produced by the finer grinding, and this is illustrated by the typical figures in Table III.

TABLE III.

TYPICAL TENSILE STRENGTHS OF BRIQUETTES MADE WITH CEMENTS OF DIFFERENT FINENESSES GROUND FROM HIGH GRADE CLINKER. THREE PARTS STANDARD SAND ONE PART CEMENT.

Residue on No. 170 Standard Mesh.	7 Days.	28 Days.
	(lb. per square inch).	(lb. per square inch).
14%	400	525
10%	425	550
5%	500	575
1%	550	625
Trace	600	650

The advantages to the user of finely ground cement may be stated as follows:

(1) A fine cement is used with greater safety because it is more constant in volume, as is shown by its behaviour under the hot tests for soundness.

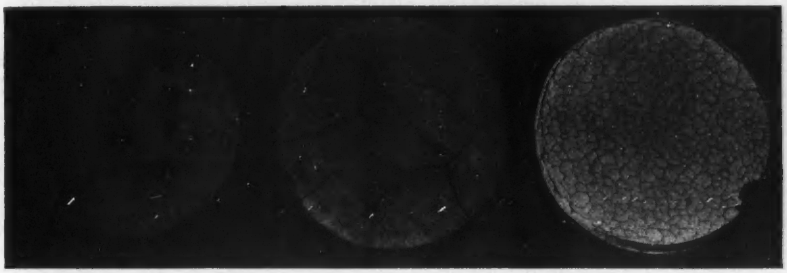
(2) Fine grinding ensures quicker hydration, as the water used in gauging acts more readily on the soluble portions of the material laid bare in greater degree by the finer grinding. It must again be mentioned, however, that cements should not be tested neat. The common tendency to develop contraction cracks when it is made into a neat paste is increased by the larger proportion of water required to make a paste with fine cement. To illustrate this point three photographs are here given of test pats (Fig. 1). No. 1 shows the neat cement pat which, when gauged, was enclosed in a damp box to set, and is thus thoroughly sound; No. 2 shows another pat of the same sound cement placed in the air to dry, and it will be seen that it has developed contraction cracks; No. 3 is a

test pat made with an unsound cement, and is given to show the characteristic difference between contraction and expansion cracks.

Mortar made with finely ground cement is found to develop considerable tensile strength in much shorter periods than a coarsely ground product, owing to the more rapid hydration.

In laying concrete floors it is naturally the aim to give an absolutely smooth and true surface, but the frequent result is that too much trowelling is done and the fine cement brought to the surface of the floor, which easily wears away and causes a considerable amount of "sanding" or "dusting." It is unwise to do so much surface trowelling, for this is undoubtedly the cause of the defect, and it may be aggravated with finely ground cements. If the surface is trowelled once only an excellent wearing surface results, and the upper layer of concrete will be from twenty to thirty per cent. stronger. In the case of the setting of a cement being interfered with by over-trowelling, then a "dusting" surface is certain to result.

There is no doubt that the character of cement residues is governed by the methods and materials used in the manufacture; it cannot be said at what point



(1) (2) (3)

Fig. 1.

of fineness grains of cement begin to have a cementitious value, but it is certain that the coarser particles in a cement hydrate far more slowly than the flour.

As illustrating the importance of particle size, the ground product from a rotary kiln has been divided into (*a*) flour; (*b*) comparatively large pieces of clinker grit retained on the No. 170 sieve; and (*c*) fine particles small enough to pass through the 170 but which are nevertheless particles of hard clinker grit. It has been shown that the fine grit (*c*), by reason of retarded hydration, gives high expansion figures under the Le Chatelier test, whilst both the flour and the inert residue (*b*) give rise to only a very slight opening of the needles of the mould.

The changes under the influence of boiling water thus observed in the three different stages of grinding were as follows:

(*a*) At the time of gauging the cement the particles of flour, so-called, were hydrated more or less completely.

(*b*) Particles of clinker grit of comparatively large size were not hydrated, except perhaps on the surface, and acted throughout as inert material.

(*c*) Particles of fine grit (clinker), which were small enough to pass the 170-mesh sieve, were only partially hydrated at the time of gauging. The cement

then set hard, but, under the influence of heat, when the block was boiled the hydration of these small particles continued with consequent expansion.

Such an experience as this would not be found to be the case with all cements, however, and an instance of this uncertainty in the results due to the expansion of the "fine grit" particles in cement has been shown in tests of other samples of rotary kiln cement, and results obtained quite contrary to those described. From these results neither the difference in fineness of grinding nor the aeration of the cements appeared to make any marked difference in the expansion as shown by the Le Chatelier method of testing for soundness.

It will be apparent therefore that, although in some cements it may be found that the "fine grit" is a dangerous and expansive element with age, yet in other cements the fine grit particles have no disturbing effect at all after aeration; so it must again be said that the function of the coarser particles in a cement is determined more by the conditions and methods of manufacture of the product than to any certain and definite result which is to be expected from all cements of whatever manufacture or process.

Since a good proportion of inert residue is now eliminated by the finer grinding of first-class cements, a mixture of sand is more than ever necessary to ensure against contraction cracks, apart from its obvious economy. Nevertheless the possibilities of economy and increased efficiency in the fine grinding of cements are by no means sufficiently appreciated even now by cement users. It is not overstating the case to say that by using a finely ground cement, with as large an admixture of sand as the circumstances will permit, the contractor's work can be carried out more satisfactorily and at less cost than with coarser cements which have nothing like the same sand-carrying capacity.

It has been shown, then, that the proportion of flour and residue contained in a cement is a matter of considerable importance, and after the percentage of each has been ascertained in a given sample an intelligent as well as an economical use of the material should follow. The following summarises the conclusions arrived at:

(1) As a general rule, the strength of concrete made from a given cement increases with the fineness of the cement for all mixtures, consistencies, gradings of the aggregates, and ages of the concrete.

(2) Finely ground cement is more effective in increasing the strength of poor rather than rich mixtures, as in the latter case the increased covering power of the fine cement is not brought into play.

(3) Fine grinding is more effective in increasing the strength of concrete at early ages than at longer periods.

(4) This bears out the accepted opinion that the coarser particles of cement hydrate more slowly, and indicates that the principal result of finer grinding is to hasten the early hardening of the concrete, a matter of importance to the engineer who, under the existing reinforced concrete regulations, is unable to take advantage of the strength ultimately attained by concrete.

(5) While increased fineness has this advantage, it is nevertheless true that chemical composition is of more importance as regards quality than fineness of grinding; *e.g.* one brand of cement with a comparatively high residue may be found to be as good in quality, or better, than another cement with a lower residue.

Thus it will be seen that the test for fineness should be directed to determining the proportion of very fine cement rather than the residue above a certain size, and this points to the way in which the fineness test should be carried out.

For the sieving test samples of cement should weigh 100 grams, and the

weight in grams of the residue remaining on the sieve represents the percentage retained by that particular sieve. A convenient size sieve for this test is about 8 in. in diameter, although square sieves are preferred by some testers owing to the greater ease with which the wire can be fixed without distortion. The manner in which the shaking is carried out determines the efficiency of the

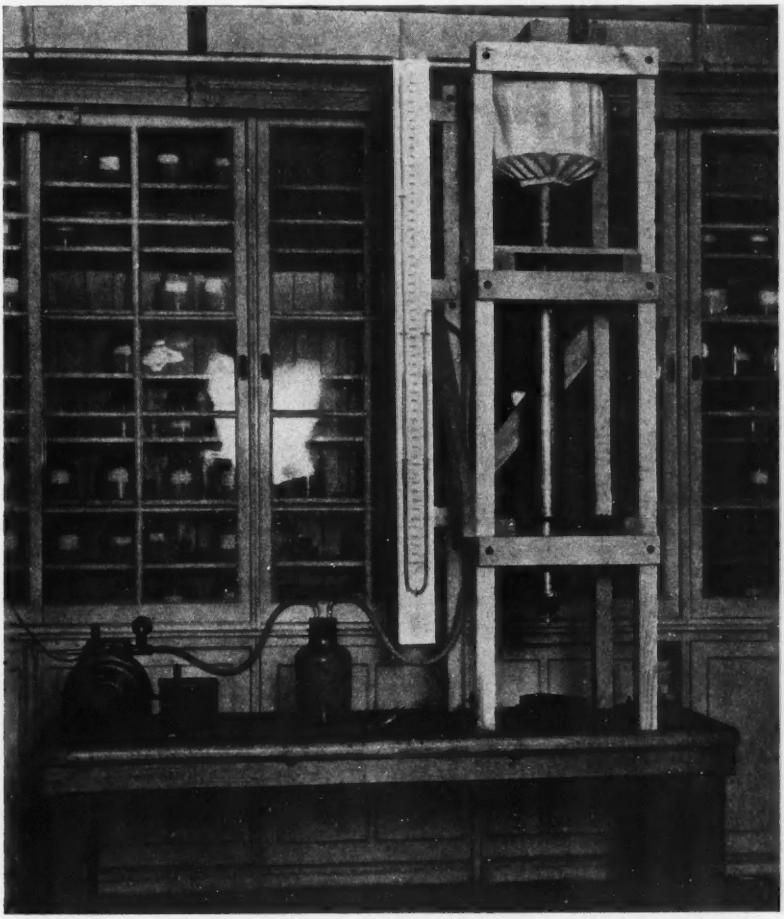


Fig. 2.

operation ; the standard time of fifteen minutes with gentle and continuous tapping of the No. 170 sieve on a table should, however, be found ample. The sieves used for the test should be frequently examined, under a magnifying glass if possible, to see that no wires are displaced leaving apertures larger than the normal, and it is hardly necessary to say that they must be kept clean.

This system of determining the fineness of Portland cement by the percentage of residue on a certain sieve has been subject to much enquiry and argument, chiefly on account of the variations found in the thickness and weaving of the wire of which the sieving is manufactured. In this country there was no general standard of size for the wire, nor was there any agreement as to how long the actual sieving process was to be continued, until the British Standard Specification for Portland Cement gave such details. The importance of the thickness of the wire used in sieve-making mainly arises from the custom of describing sieves by the number of meshes per lineal inch, but the size of the aperture is, of course, the determining factor.

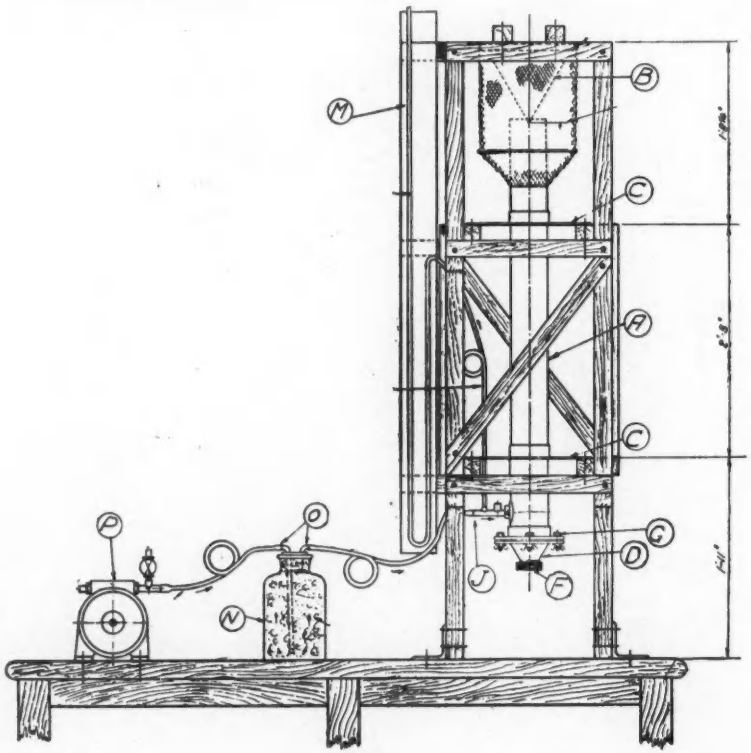


Fig. 3.

Since, however, it is desirable to know the percentage of actual flour in a given sample according to the different classes of grinding machines used in the process of manufacture, an apparatus has recently been devised for this purpose, and is illustrated in Figs. 2, 3, and 4. The machine was designed with a view to putting the estimation of the flour content on a "quantitative" basis, and is known as the Standard Elutriator. The principle of this instrument is simple. A definite amount of cement is "washed" free from "flour"

by a current of air, and the non-flour residue is weighed; the difference between the original and the final weights gives the proportion of flour present.

Various machines for determining the percentage of flour have been in use for some years, but they are all quite arbitrary and the "flour" is not the same in proportion or particle size in any two of them. Many of these machines depend in principle upon air elutriation of the particles, but the quantity of material lifted by an air stream is governed by the size and weight of the particles and the velocity of the air. As the instruments referred to work at different and generally unknown velocities, the percentage of "flour" is merely that portion of the cement that happens to be elutriated in the particular machine. For example, a sample of cement tested under standard conditions by two different

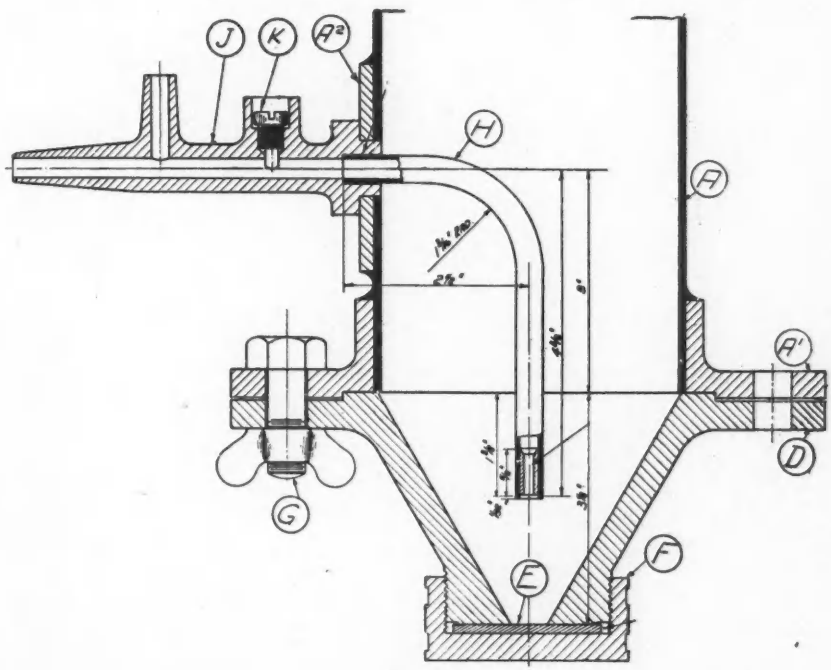


Fig. 4.

flourometers contained 79.5 per cent. of flour by one machine and 71.0 per cent. by the other.

The Associated Portland Cement Manufacturers, Ltd., have adopted a "standard flour" in cement as the material elutriated by air at a definite velocity of 21 ft. per minute. The average particle diameter of this standard cement flour is approximately 0.01 mm., and varies but little if elutriated at a velocity of 21 ft. per minute. The quantity of the material elutriated at this velocity is a direct measure of the fineness of the cement, and partially of its hydraulic value. Hence, a direct comparison can be made of cements of different makes.

The Standard Elutriator (previously referred to) now in use at the factories of the Associated Portland Cement Manufacturers, Ltd., is of the down-blast type, the air under pressure blowing into the apex of an inverted cone, thus agitating and separating the particles as well as maintaining a steady upward velocity in the elutriating tube. The apparatus (Figs. 2, 3, and 4) consists of a brass tube (A) 4 ft. long and 4 in. internal diameter, closed at the lower end by an air-tight machined brass cone (D) with renewable steel apex plate. The tube is mounted in a suitable stand carrying a manometer and a deflecting cone (B), the point of which projects $\frac{1}{4}$ in. into the mouth of the tube (A). The upper rim of this cone is formed to carry a flannel bag or filter to retain the fine dust elutriated. Air is blown into the apparatus from a small motor blower (P), through an oil trap (O) and a nozzle (J, H) which enters the elutriating tube near the bottom, and, bending downwards through the centre of the tube, terminates with an $\frac{1}{8}$ in. diameter jet inside the bottom cone (D). The air-inlet tube is provided with a tubulure for attachment to the manometer, and an adjusting screw (K) for calibration purposes. Once calibrated, the screw (K) is hermetically sealed and not afterwards disturbed unless recalibration becomes necessary.

The rotary blower is fitted with a relief orifice controlled by a wheel valve, the adjustment of which enables a constant pressure to be maintained in the manometer. Jigs are provided to ensure that the nozzle and jet are assembled centrally in the elutriating tube and cone.

The test is made by placing 33.3 grams of the cement to be examined in the bottom cone, which is securely fixed to the elutriating tube by means of the wing nuts (G). A machined recess in the base of the tube enables an air-tight fit to be made without the use of rubber or other washers. The relief valve being fully open, the motor is started and the valve gradually closed until the difference in level in the two limbs of the manometer is 41.5 inches. Blowing at this pressure is continued for 25 minutes, when the motor is stopped and the cone detached from the stack. The residue in the cone, which should be dark-coloured, clean grit, and free from dust, is brushed out and weighed. The difference between this weight and the 33.3 grams of cement taken for the experiment represents the weight of flour removed by the operation. Provided the pressure is maintained at 41.5 inches of water the air velocity in the elutriating tube remains at 21 ft. per minute, at which velocity standard flour is carried over.

Certain precautions are necessary for accurate work:—

(1) The test should be made in a room with a reasonably dry atmosphere and of equable temperature. Cement flour has a great affinity for moisture, and damp air may cause the flour to stick in the tube or clog the filter. If the room is hot at one time and cold at another the accuracy of the results will be affected owing to variations in the volume of air in the elutriating tube.

(2) Flour should not be left long in the flannel filter. The filter should be emptied and shaken at least daily.

(3) With very fine cement containing 80 per cent. or more of standard flour it is generally advisable to tap the tube and cone occasionally during the operation to assist the air stream in agitating and separating the particles. It is also necessary to tap the tube before beginning a test to ensure that no flour from a previous test is adhering to it.

(4) Care must be taken that the nozzle and jet are not damaged or displaced from the central position in the cone.

With these precautions the instrument is capable of giving results to 0.5 per cent. or less in the hands of different operators.

Notes from the Foreign Press.

The Reaction between Kaolin and Lime on Static Heating. I. Weyer. *Zement*, Vol. 20, pp. 560, 608, 692, 1931.

Mixtures of kaolin and $CaCO_3$ (mostly 1 mol. kaolin to 16 mol. CaO) were heated at various temperatures for long periods in an electric furnace, and the reaction studied chemically and microscopically. The temperatures of the various reactions were found to be considerably lower than those obtained with mixtures of pure oxides. The speeds of reaction are mainly dependent on the rate of diffusion of lime through the reaction product, but are also influenced by grain size.

The reaction begins between 500 and 600 deg. C., at which temperature the $CaCO_3$ is already completely dissociated. $CaO.Al_2O_3$ is first formed; at 700 deg. the formation of $\beta 2CaO.SiO_2$ begins; 700 deg. appears to be the characteristic temperature of the beginning of silica combination. $\beta 2CaO.SiO_2$ formation is completed between 700-1300 deg.; this is the only modification formed, and does not "dust." Absence of $\beta 2CaO.SiO_2$ must therefore not be deduced from failure to "dust." $\alpha' 5CaO.3Al_2O_3$ is formed at 950 deg., and is converted into $3CaO.Al_2O_3$ without passing through the stable modification. $3CaO.Al_2O_3$ formation begins at 1000 deg. C., but is not rapid until higher temperatures are reached. $3CaO.SiO_2$ formation begins with considerable velocity at 1300 deg. and is complete at 1350 deg., when the reaction product is an aggregate consisting mainly of tricalcium silicate and aluminate; this is not affected by further heating to 1400 deg. Tricalcium silicate is alite. Crystals of the compound were obtained and investigated.

In the course of the work experiments were carried out with kaolin previously burnt to various temperatures, but Tammann and Pape's result that burnt kaolin reacts more intensively with lime than normal kaolin could not be confirmed.

The Boiling Test. H. Luftschitz. *Zement*, Vol. 20, p. 585, 1931.

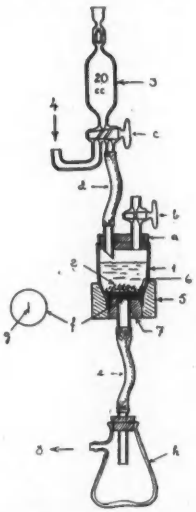
The mechanism of the boiling and kiln tests depends upon two opposing forces, (1) that of the water and steam inside the pat endeavouring to find an exit, (2) that due to the contraction of the pores of the cement gel as a result of heating. This gives rise to a network of cracks in the case of the boiling test and to peripheral cracks in the kiln test. Pats of neat cement 24 hours old are impermeable to water and the surrounding water does not penetrate into the test-piece in the boiling test. As a result of these considerations it is suggested that the boiling test (German) and the kiln test (Austrian) should be replaced by a test in which pats of 1 : 3 standard mortar are subjected to a temperature of 70 deg. C. for four hours, wrapped in a moist cloth.

Colloidal Cement Hardening. H. Kühl. *Zement*, Vol. 20, p. 650, 1931.

In continuation of earlier work (see CEMENT AND CEMENT MANUFACTURE, June, 1930, p. 837) on the preparation of cement hardening without crystallisation, a melt of percentage composition SiO_2 26.9, Al_2O_3 12.9, CaO 50.2, was prepared and quenched in water; this showed no trace of crystalline structure. The ground melt was gauged with KOH solution and gave tensile strength 411 lb. per sq. in. after 28 days' air storage. Microscopic examination showed only a trace of crystalline structure between crossed Nicols at 28 days, and X-ray examination showed no trace of crystalline structure. Tests with ground gypsum admixtures showed that the X-ray method was capable of detecting 2 per cent. of crystalline matter. It is thus proved that good hydraulic strength can be attained as a result of purely colloidal phenomena.

Water Solubility of Cements. D. Werner. *Zement*, Vol. 20, p. 626, 1931.

An apparatus for determining the water solubility of set cement is described. The cement test-piece is powdered and sieved. One gramme of the fraction of particle size 0.200-0.088 mm. is placed in a glass filter crucible (see figure). The rubber sheet *f*, fixed firmly below the filter, contains a slit *g*, which only opens when vacuum is applied. Twenty cc. distilled CO_2-free water are run in from the automatic burette 3, with cock *b* open; *b* is then closed and the crucible shaken in a shaking machine for 5 minutes. *b* is then opened, flask *h* is evacuated, and the liquid sucked from the filter is collected. The solids in solution are then analysed. The quantity of water and time of shaking are such that equilibrium between the solid and liquid phases is reached. The process is



repeated a number of times and the total amounts of CaO, etc., extracted are plotted against the number of extractions.

A Portland cement, with and without additions of As_2O_3, and an aluminous cement, were submitted to this process. For Portland cement there is rapid initial solution followed by a much slower stage. During the rapid stage 0.1 g. CaO per 1 g. cement is dissolved; solution of SiO_2, R_2O_3, etc., is relatively slight. With additions of 30-40 per cent. As_2O_3, solution of all constituents is very slight, but above this value As_2O_3 solution rapidly increases. The results with pure aluminous cement are similar to Portland, but in this case about equal parts CaO and Al_2O_3 are dissolved. See also CEMENT AND CEMENT MANUFACTURE, Oct., 1931.

Determination of Silica in Cements. F. Waclaw. *Zement*, Vol. 20, p. 759, 1931.

The following rapid method can be used for cements and slags, but not for raw materials. Mix 1 g. cement in a covered beaker with 2 cc. water and add 10-15 cc. 70 per cent. perchloric acid. Boil for five minutes, cool slightly, dilute carefully with hot water, add a little HCl, and filter hot. Wash the SiO_2 precipitate well with boiling water to remove perchloric acid, and ignite as usual.

R_2O_3 and CaO can be determined in the filtrate by the standard methods. By this method the SiO_2 can be separated and filtered in fifteen minutes. It is accurate enough for works control, but for the highest accuracy the standard method should be used.

Effect of Additions to Portland Cement on its Mechanical Properties. P. P. Budnikoff and M. I. Nekritsch. *Zement*, Vol. 20, p. 694, 1931.

In continuation of the authors' earlier work, 0.1-1 per cent. of fluorspar, phosphorite, superphosphate and waste gypsum (pottery moulds, both heated to 180 deg. C. and unheated), and 0.5-5 per cent. of clay burnt at various temperatures, were added to Portland cement. Except for fluorspar none of these materials had an appreciable effect on strength. Additions of fluorspar resulted in increased crushing strength, the best results being obtained with 0.1 per cent.:

	Crushing strength. (lb. per sq. in at 28 days.)	Tensile strength.
1 : 3 mortar without addition ..	3,380	388
With 0.1 per cent fluorspar ..	4,539	388
With 1.0 per cent fluorspar ..	3,812	408

Is Calcium Chloride of Equal Value to Gypsum as an Addition to Clinker? O. Frey. *Zement*, Vol. 20, p. 696, 1931.

A rotary kiln cement was tested (1) without additions, (2) with 2-3.5 per cent. $CaCl_2$, (3) with 1.5-3 per cent. gypsum, (4) adding 3-6 per cent. $CaCl_2$ to the mixing water, using gypsumised cement.

It was found that gypsum is by far the most satisfactory medium for regulating setting time, and gives higher strengths than $CaCl_2$. The hygroscopicity of $CaCl_2$ is a further serious disadvantage. Maximum strengths were obtained with 2 per cent. both of $CaCl_2$ and of gypsum, as follows:

	Crushing strength. (lb. per sq. in. at 28 days.)	Tensile strength.
Cement without additions ..	7,864	587
With 2 per cent. $CaCl_2$	7,821	411
With 2 per cent. gypsum.. ..	9,527	540

Additions of gypsum plus $CaCl_2$ gave lower values than the gypsum alone. Additions of $CaCl_2$ to the mixing water had little effect on strength.

Report of the Kiln Commission of the Association of German Portland Cement Manufacturers for 1930-31. E. Schott. *Zement*, Vol. 20, p. 754, 1931.

(1) Test on a Lepol kiln, consisting of an old 92-ft. rotary kiln, 10 ft. dia., combined with a travelling grate 26 ft. long by 10 ft. wide. The raw meal contained 12.8 per cent. moisture. The heat consumption was 193,950 B.T.U. per 100 lb. clinker. The gas temperature above the travelling grate was 841 deg. C., and 155 deg. behind the grate; 13.4 per cent. CO_2 (on the dry material) was removed from the material on the grate. Dust extraction was effective. The output of clinker was 153 cwt. per hour.

(2) Test on an Andreas automatic shaft kiln. The raw material contained 13.9 per cent. moisture. Heat consumption 210,852 B.T.U. per 100 lb. clinker. Average exit gas temperature 260 deg. C., the instantaneous values rising at times above 400 deg. The exit gases did not contain carbon monoxide. The output of clinker was 115 cwt. per hour.

Effect of Additions to Cement Raw Meal containing Blastfurnace Slag. By M. Paschke and W. Meyer. *Zement*, Vol. 20, p. 850, 1931.

The effect of adding burnt pyrites, fluorspar, NaCl, KCl, $CaCl_2$ and granulated slag (in quantities varying from 0.3 to 3.0 per cent.) to a slag cement raw mix

(composed of limestone and granulated slag) was investigated. The cements were burnt in a large crucible in a coke-fired furnace. The reducing conditions naturally affected the properties of the resulting cements, in which all the iron was present as FeO. The cements were tested both as burnt and as an iron-Portland cement (70 parts clinker, 30 parts slag).

In general all these materials had a favourable influence on the ordinary Portland cement when the additions did not exceed 0.3 per cent. The results were still better with the iron-Portland cement, in which additions up to 0.6 per cent. improved the properties. The best results were obtained with $CaCl_2$, which, however, showed a decided tendency to expansion; this could be rectified by the slag additions for proportions of $CaCl_2$ not exceeding 1 per cent. After $CaCl_2$ come KCl and NaCl (not more than 0.3 per cent.). NaCl also shows a tendency to expansion, which can be entirely rectified by slag. Fluorspar should be used with extreme care, as more than 0.3 per cent. may cause serious reductions in strength. Burnt pyrites gave the worst results, but even here 0.3 per cent. gave increased strength.

Fine Grinding and the Strength of Cement. W. Weisberger. *Tonind. Zeit.*, Vol. 55, pp. 933, 946, 1931.

Further light is thrown upon the opposing results obtained by Helbig and Steiner (that strength continuously increases with increased fineness of grinding) and of Kühl (that up to a certain limiting fineness strength increases, but falls off on still continuing the grinding). Kühl has not allowed for the reduction in strength due to increasing the quantity of mixing water. With a

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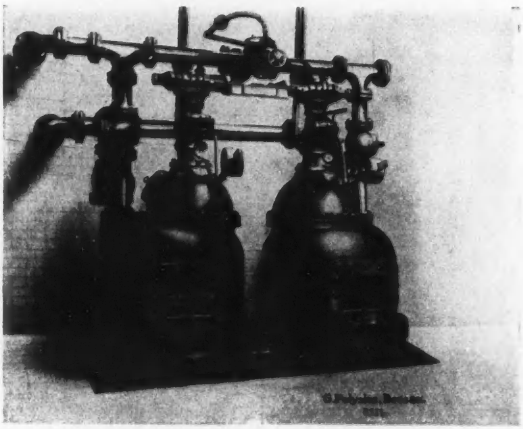
cement of given fineness the strength first of all increases to a maximum and then decreases as the mixing water is increased. For a given water content the strength continuously increases with increased fineness. In Kühl's experiments the test-pieces were mixed to a given consistency, *i.e.*, as the fineness increased the amount of water required increased. The consistency adopted lay upon the downward branch of the water content-strength curve. With the coarser cements the increase of strength with fineness had a greater effect than the decrease of strength due to increase in the mixing water; there was thus a net increase in strength. As fineness increased, however, the effect of the increased mixing water preponderated, and there was a net reduction in strength as the material became finer. The reason that Kühl's result is not obtained by other workers is as follows. With some cements the amount of water required for earth-moist consistency lies on the rising branch of the water content-strength curve, so that both increase in fineness and increase in water cause increase in strength. If the experiments were repeated with such cements using plastic or wet consistency the Kühl effect would be obtained.

It may be accepted that the absolute maximum strength continually increases as the material becomes finer, approaching a maximum asymptotically.

Slurry Transport Pump.

The illustration below shows a slurry transport pump known as the "Double-Pressor," manufactured by Messrs. G. Polysius, A.G. A special feature of this pump is that the actuating devices do not come into contact with the material



"Double-Pressor" Slurry Pump.

to be conveyed, and in consequence there are no excessive welding costs. An illustration of a "Cera-Pump" made by the same firm was given on page 15 of our January number; this is a pump for the conveyance of raw-meal, coal dust and cement, and is also driven by compressed air.

Trade Notices.

Oil Engines.—The economy and durability of oil engines as prime movers is proved by a new brochure (Publication No. 6270) issued by Messrs. Ruston and Hornsby, Ltd., of Lincoln, in which the claims of the manufacturers of the well-known Ruston cold-starting oil engine are substantiated by independent figures of costs. It is shown, for instance, that the average total engine cost per unit of electricity generated by these engines is 0.517d. These independent observations, over a very large number of engines of various makes, show that the cost of lubricating oil for Ruston engines is only 0.039d. per unit generated, and the cost of fuel 0.247d. per unit; the average price of fuel used for these engines was only 66s. 9d. per ton. This well-produced brochure, which contains a wealth of data of use to all power users, will be sent on application to Messrs. Ruston and Hornsby, Ltd.

Excavation for Lloyd's Barrage.—The construction of Lloyd's Barrage is of particular interest in that the bulk of the excavation, amounting to more than twice the excavation for the construction of the Panama Canal, was entrusted to dragline excavators. Forty-six machines, all made by Messrs. Ruston-Bucyrus, Ltd., of Lincoln, were used, including nine machines weighing about 350 tons each, and digging eight to ten tons of material at a bite, at the rate of more than one bite a minute. These large machines were capable of digging in one operation, without rehandling, canals up to 300 ft. bed width. Construction costs have been reduced, and the canals have been dug to an exact time schedule. A pamphlet on the Sukkur Barrage, written by one of the staff of Messrs. Ruston-Bucyrus, Ltd., who spent several years in collaboration with the Chief Engineer during the construction of the barrage, describes the work of the machines, and gives an accurate account of the working costs; copies of this useful brochure may be obtained from the company.

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